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ROHM & HAAS COMPANY

REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

REPORT NO., S-83

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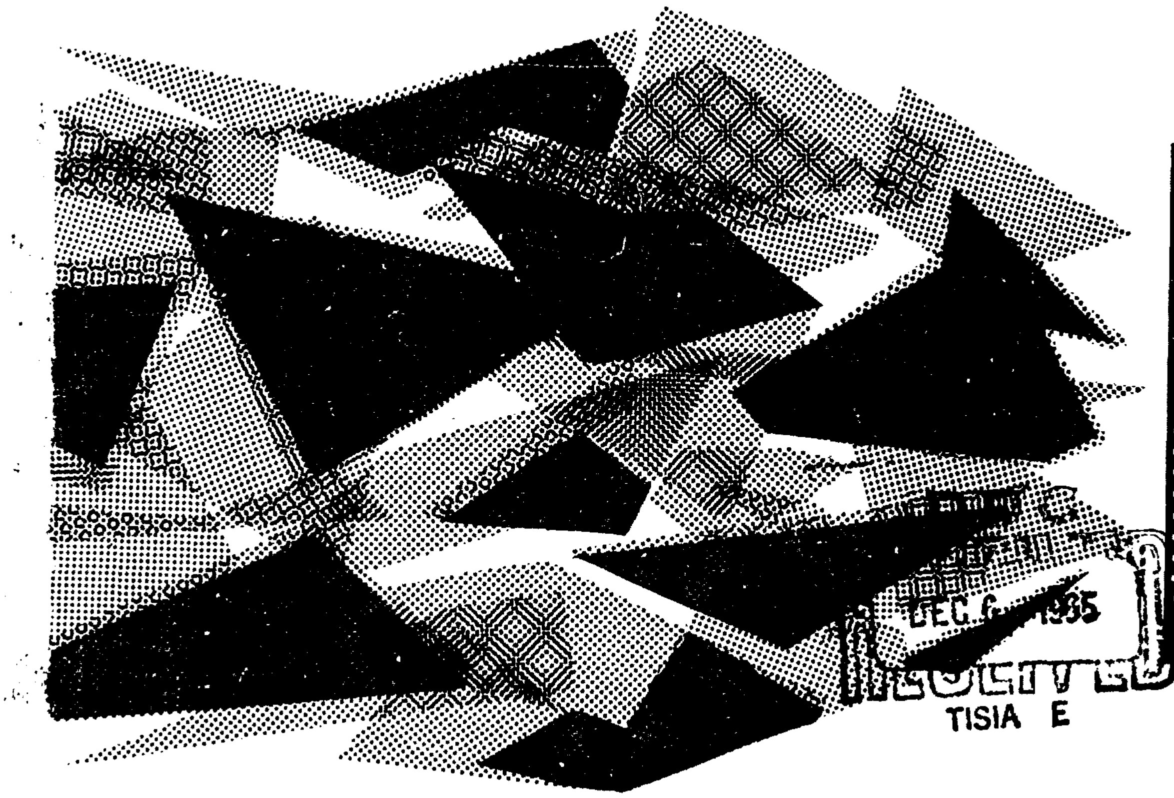

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Report No. S-83

SCALE-UP N_2F_4-OLEFIN REACTIONS IN A HIGH PRESSURE LIQUID PHASE FLOW REACTOR (C)

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ABSTRACT

Difluoramino compounds were continuously synthesized by the high pressure liquid phase reaction of N_2F_4 with an olefin diluted in an appropriate solvent. About 400 pounds of two N_2F_4 adducts were synthesized over a two-year period in a tubular reactor operating in the laminar flow regime. The productivity of the reactor was progressively increased to a rate of about 100 pounds per month. A mathematical model of the flow reactor was developed and used to establish reaction conditions that would not result in prohibitive exotherms.

GLOSSARY

TVOPA	-	1, 2, 3-Tris[α,β-bis(difluoramino)ethoxy]propane
A-3	-	2, 3-bis(difluo- nino)propyl formate
NFPA	-	2, 3-bis(difluoramino)propyl acrylate
Freon TF	-	1, 1, 2-trichloro-1, 2, 2-trifluoroethane
Freon MF	-	trichlorofluoromethane
2D	-	Refers to two-dimensional mathematical model
D/P cell	-	Pneumatic differential pressure cell with integral flow nozzle

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1. INTRODUCTION

Composite solid propellants based upon binders and plasticizers containing the difluoramino (NF_2) group have been of interest for the past decade. Difluoramino compounds which have been scaled-up to the pilot plant by these Laboratories were based on the addition of tetrafluorohydrazine (N_2F_4) to olefins by the reaction shown in Eq. (1). The first pilot plant unit

$$\gt C = C \lt \quad + \quad N_2F_4 \longrightarrow -\underset{NF_2}{\overset{|}{\underset{|}{C}}} - \underset{NF_2}{\overset{|}{\underset{|}{C}}} - \qquad \Delta H_R \approx -35 \, \frac{k\,cal}{g\ mole} \qquad (1)$$

was a continuous vapor phase tubular reactor operating at atmospheric pressure, and production rates up to 150 gms/hr[1] were obtained. Although the vapor phase reactor was useful in various programs, vapor phase addition was impractical for the synthesis of many NF plasticizers because neither the olefin nor product was easily vaporized.

This report describes the design and successful demonstration of a liquid phase reactor unit suitable for the continuous production of non-volatile compounds by the exothermic N_2F_4-olefin reaction. The contacting technique chosen was the absorption of N_2F_4 into a solvent-olefin mixture at 400 - 500 psig. A similar principle had been demonstrated by Rohm & Haas Company for continuous vinylation of alcohols with acetylene.[2] DuPont[3] constructed an experimental unit to show the feasibility of using a continuous

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[1] Rohm & Haas Company, Quarterly Progress Report on Chemical and Propellant Processing, No. P-63-17, January 15, 1964.

[2] Nedwick, John J., Ind. Eng. & Chem., Process Design & Development, 1, 1962, 137.

[3] E. I. du Pont de Nemours & Company, Supply of Experimental High-Energy Solid Propellant Materials, Final Report No. DP-504, July 1, 1962 through September 30, 1963.

tubular reactor for the liquid phase addition of N_2F_4 to olefins, but their unit required batch work-up of the product. The liquid phase reactor installed here provided for continuous work-up (desorption of unreacted N_2F_4) as well as continuous reaction.

Although design of the liquid phase reactor emphasized the capability of synthesizing a large variety of possible adducts, only two have been synthesized in large quantities to date. About 190 lbs. of 2,3-bis(difluoramino)propyl formate (A-3) was made by addition of one mole of N_2F_4 to allyl formate according to reaction (2) and about 215 pounds of 1,2,3-tris[α,β-bis-

$$H_2C = CH - CH_2 - O - \overset{\overset{\displaystyle O}{\|}}{C}H \;+\; N_2F_4 \longrightarrow H_2\underset{\underset{\displaystyle NF_2}{|}}{C} - \underset{\underset{\displaystyle NF_2}{|}}{C}H - CH_2 - O - \overset{\overset{\displaystyle O}{\|}}{C}H \qquad (2)$$

(difluoramino)ethoxy]propane (TVOPA) was made by the addition of three moles of N_2F_4 to trivinoxypropane (TVOP) according to reaction (3).

$$3\,N_2F_4 \;+\; H_2C = CH-O-CH\,(CH_2 - O - CH = CH_2)_2 \longrightarrow$$

$$H_2\underset{\underset{\displaystyle NF_2}{|}}{C} - \underset{\underset{\displaystyle NF_2}{|}}{C}H - O - CH\,(CH_2 - O - \underset{\underset{\displaystyle NF_2}{|}}{C}H - \underset{\underset{\displaystyle NF_2}{|}}{C}H_2)_2 \qquad (3)$$

The A-3 [an intermediate in the synthesis of the propellant binder, 2,3-bis-(difluoramino)propyl acrylate (NFPA)] was formerly synthesized in the continuous vapor phase reactor. The TVOPA was of interest as a plasticizer for the same system. Some of the properties of A-3 and TVOPA are summarized in Appendix A.

2. CONCLUSIONS AND RECOMMENDATIONS

1. The feasibility of the continuous liquid phase synthesis of N_2F_4 adducts in a tubular reactor operating in the laminar flow regime was successfully demonstrated.

2. Mathematical models were used to characterize the reaction exotherms, and explosive reactions were avoided.

3. Scale-up to higher production rates is practical and necessary to the pilot plant program, but this will be seriously restricted in the laminar flow regime.

4. Further studies should be made for scale-up to production in the turbulent flow region.

3. DISCUSSION

3.1 Advantages of the Liquid Phase Flow Reactor

Use of the liquid phase reactor to prepare N_2F_4 adducts has several advantages compared to a vapor phase reactor. As shown in Table I, these advantages are related to the increase in reaction rate caused by the high reactant concentration in the condensed phase. The advantages of the liquid phase reactor include:

(1) a substantial reduction of reaction temperature with maintenance of reasonable reaction rates for relatively volatile olefins and adducts;

(2) a high yield per unit volume of the reactor due to the high concentration of reactants in the liquid phase;

(3) the extension of continuous flow reaction to non-volatile systems which otherwise would require autoclave operation. This consideration was particularly important for propellant plasticizers, for which low vapor pressure was an essential requirement.

Table I

Comparison of Liquid and Vapor Phase Reactors in A-3 Synthesis

	Liquid Phase Reactor	Vapor Phase Reactor
Reactor Temp., °C	103 - 130	210
N_2F_4 inlet concentration, moles/liter	1.5	0.03
Space-time yield, moles/liter-hr.	3.0	0.3

3.2 Operation Summary

A two-stage reactor operating in the laminar flow regime was used for the synthesis of A-3 and TVOPA. The reactor coils were immersed in a boiling water bath. The N_2F_4 was absorbed at an elevated pressure upstream of the first stage. Typical reaction conditions for both TVOPA and A-3 are summarized in Table II.

Table II

Summary of A-3 and TVOPA Operating Conditions

	A-3	TVOPA
Production rate, gms. per hour	425	400
Yield on olefin/recovery, %	90-99+	94-99+
N_2F_4 concentration, gms/cc solvent	0.2	0.2
Solvent	Freon TF	80% Freon TF, 20% chloroform
N_2F_4:olefin mole ratio	1.05-1.10	3.2-3.3
Reactor pressure, psig	400-450	400-450
Reactor temperature, °C		
Stage I	103	85
Stage II	125-130	115
Reactor volume, ml		
Stage I	311	311
Stage II	425	425
Residence time, minutes	≈28	≈25
Pounds/shift, maximum	6.3	6.0

The N_2F_4 concentration was normally 0.2 grams/cc solvent, resulting in product diluted with 85% solvent. Freon TF (CCl_2F-$CClF_2$) and a mixed solvent, 80% Freon TF and 20% chloroform, were used as the diluents for A-3 and TVOPA synthesis, respectively. The total residence time in both stages was about 25 minutes. Reaction pressures were varied from 400 to 500 psig with no noticeable effect on conversion or product quality.

Two mathematical models of the reactor were developed, the bulk model and the two dimensional model (Section 3.5). Figure 1 shows the calculated conversions and exotherm profiles for the TVOPA production conditions listed in Table II. Both models indicated a conversion of about 97% and a maximum exotherm of 8-12°C in each stage. About 50-60% of the reaction was carried out in the first stage at a nominal temperature of 85°C, and the

reaction was completed in the second stage at a nominal temperature of 115°C. Experimentally measured conversions were within the range predicted from the theoretical models.

Typical analytical values[1] for TVOPA produced in the flow reactor are shown in Table III. Occasional batches had N-fluoroazoxy concentrations greater than 1% because of high (>0.3%) nitric oxide levels in the N_2F_4. The source of the alcohol impurity was undetermined, and the impurities corresponding to some of the other infrared absorbance frequencies were not fully identified. Specifications on raw materials used in the synthesis of TVOPA and A-3 are shown in Appendix B.

The two N_2F_4 adducts were synthesized alternately during the 1-3/4 year period since the flow reactor was put into operation. Productivity for each reaction was increased to about 0.9 pounds per hour. In a recent calendar month 79 pounds of TVOPA was made using a single shift operation. Operation was relatively trouble-free and down time required for equipment repair was reduced to less than 20% of the total operation time.

The liquid phase flow reactor was designed for a maximum production rate of about one pound per hour, corresponding to a Reynolds number of about 400. Further scale-up appears practical within the laminar flow regime, and equipment has been obtained to increase the capacity to about three pounds per hour. Additional mathematical characterization is required for turbulent flow where the heat transfer rate would be considerably higher, and hence more favorable for further increased reaction rate.

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[1]Test details are reported in Rohm & Haas Company, Quarterly Progress Report on Chemical and Propellant Processing, P-64-10, January 22, 1965.

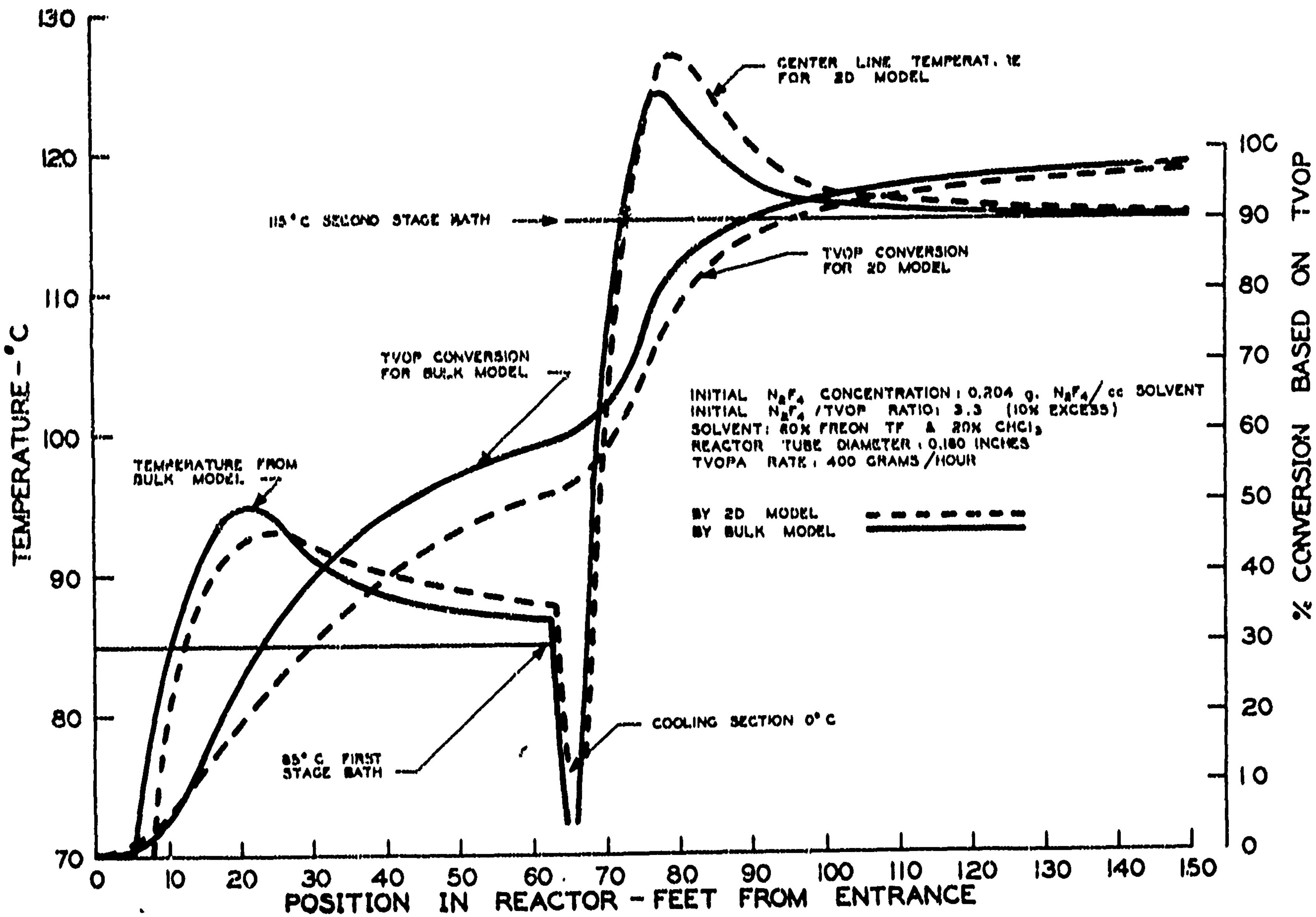

FIG. 1 CALCULATED TEMPERATURE AND EXOTHERM HISTORY FOR TVOPA PRODUCTION IN A TWO-STAGE REACTOR

Table III

Quality Control Tests on TVOPA

	Typical Range[a]
I. Infrared Analysis	
A. %	
2.78μ - (alcohol as ethanol)	0.07 - 0.045
6.60μ - (N-fluoroazoxy as pentakis adduct)	0.10 - 0.45
6.10, 6.18μ - (residual olefin as TVOP)	nil - trace
B Absorbance Units	
5.78μ (carbonyl	0.025 - 0.045
5.92μ (fluorimino)	0.125 - 0.150
6.23μ (fluorimino)	0.040 - 0.085
II. Differential thermal analysis (10°C/min)	
Start, °C	160 - 185
Peak, °C	260 - 270
III. Difluoramino content[b]	
Ferrous reducibles, meq/ml	36.5 - 37.5
IV. Impact sensitivity	
Picatinny, kg cm (RDX = 10.5 kg-cm)	10.9 - 25.3

(a) Typical values found for TVOPA synthesized from N_2F_4 greater than 99.5% assay.

(b) Test is described in Rohm & Haas Company, Advanced Propellant Synthesis Report No. S-59, March 31, 1965.

3.3 Apparatus

A flow sheet of the system, which was designed for the completely remote control of the N_2F_4 pressurization, reaction, depressurization, and continuous work-up, is shown in Fig. 2. (A detailed description of each section is included in Appendix C.) Gaseous N_2F_4 was metered with a two-stage diaphragm compressor from a storage cylinder to a mixing tee for absorption into the solvent-olefin solution. The N_2F_4 metering was automatically controlled by a closed-loop pneumatic system consisting of a differential pressure meter, a two-mode set point controller, and a pneumatic stroke controller on the first stage of the compressor. The solvent and olefin were premixed and metered by a positive displacement pump. Because the heat of solution of N_2F_4 in the solvent is 4 to 6 kcal/mole,[1] the absorption and mixing were accomplished in a cooled section of the pipe line. The three-component solution was fed to the two-stage tubular reactor, which was maintained at an elevated pressure by the downstream application of nitrogen pressure on the domes of two Grove Mity-Mite let-down valves, which were mounted in series. Prior to depressurization through the let-down valves, the reactor effluent was cooled to less than 20°C. The unreacted N_2F_4 was continuously desorbed from the depressurized liquid with a nitrogen sweep in a countercurrent wetted wall column. The product was collected in another bay following an air sparge in a hold-up vessel. The air-N_2F_4 laden nitrogen was further diluted with nitrogen and discharged through a 2-inch aluminum stack at 50 feet above ground level.

Each reactor stage consisted of a coil of 0.180-inch I.D. tubing totally immersed in a liquid water bath contained in a totally enclosed 6-inch pipe. The system was designed for a reaction pressure up to 500 psig, temperatures from 20 to 170°C, and production rates up to about one pound per hour of adduct.

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[1]Rohm & Haas Company, Quarterly Progress Report on Physical Chemistry, P-62-25, April 1963.

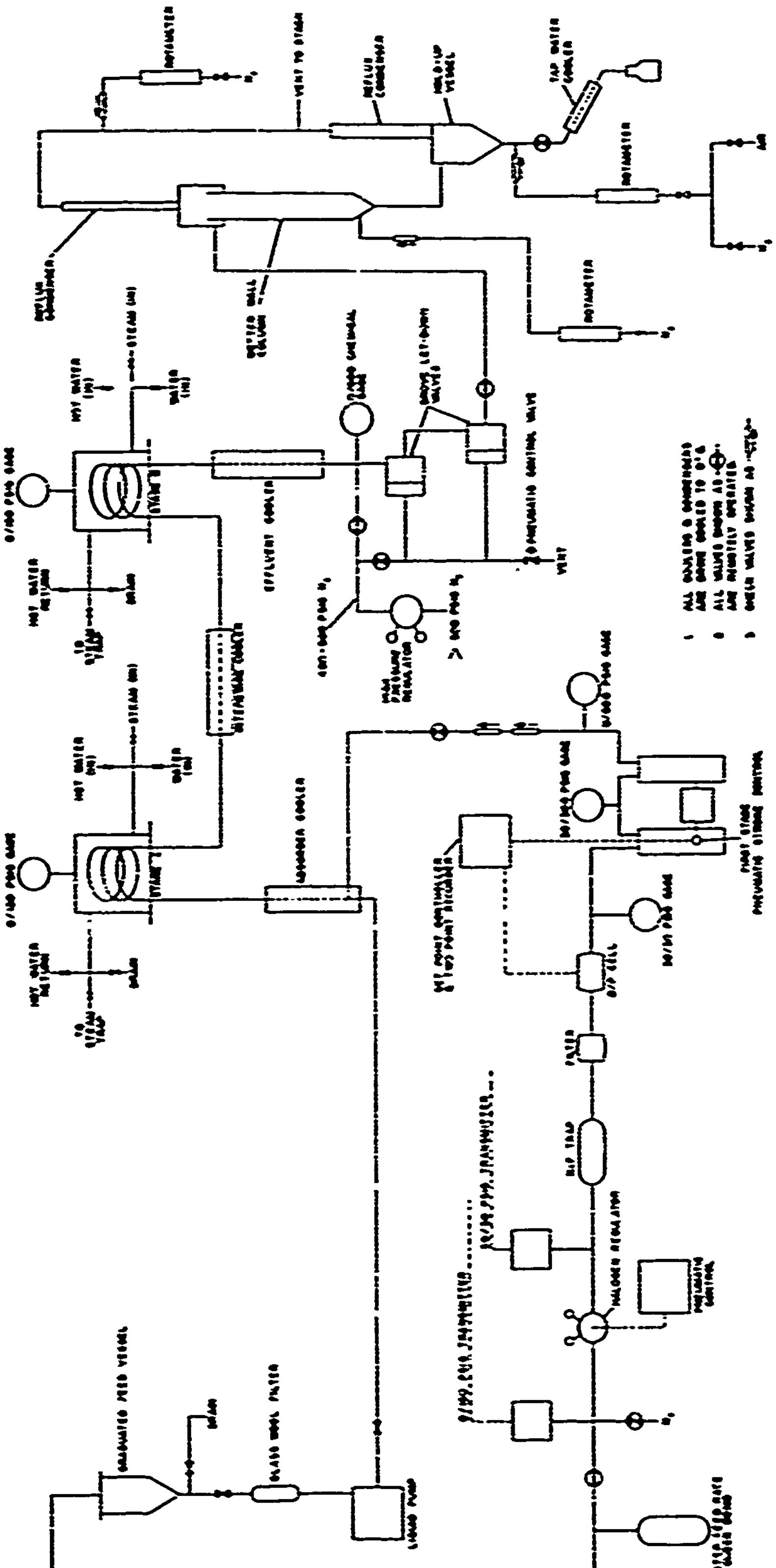

FIG. 2 FLOW DIAGRAM OF LIQUID PHASE REACTOR

3.4 Operating Techniques

The detailed standard operating procedure is included in Appendix D.

During the steady-state portion of the batch, operational requirements were mainly limited to checking and adjusting process variables, including N_2F_4 feed rate, N_2F_4 suction pressure, olefin solution feed rate, stage temperatures, and nitrogen and air flows to the product collection system. About 6-1/2 to 7 hours of steady-state operation was possible for a single shift. The process was controlled by one operator during this period. Typically, the start-up, which was limited to equipment checkout and filling out batch cards, consumed about 15 minutes. The shut-down took about 45 minutes, the period required to flush the reactor with one reactor volume of chloroform, which was collected with the product. For personnel entry into the reactor bay the shut-down procedure was extended to include flushing the N_2F_4 from the compressor manifold with nitrogen, which added 15 minutes to the shut-down.

Before each start-up the N_2F_4 compressor manifold and the reactor coils were leak checked by pressurization and holding, usually overnight, but for at least 15 minutes. No pressure drop was acceptable in either section, and a leak-free system was easily maintained. Because air can initiate an explosive N_2F_4 reaction, special precautions were taken to insure that air was completely purged from the system. For start-up following the simple overnight shutdown, the purge procedure was usually not required. If air was admitted to a section, the N_2F_4 compressor manifold was flushed with nitrogen and the solvent-olefin feed line as well as the reactor coil were flushed with solvent.

3.5 Exotherm Characterization

The addition of N_2F_4 to olefins is highly exothermic, and the product is subject to thermal degradation. Therefore, exotherm control was a serious consideration in the reactor design and operation.

Two mathematical models[1,2,3] of the coupled heat transfer-reaction rate process in the flow reactor were developed to identify possible hazardous operating conditions and predict the effect of changes in the operating conditions on exotherms and conversions. The models (for laminar flow operation) were:

(1) The bulk model, which assumed a slug flow profile with concentrations and temperatures varying only along the tubular axis.

(2) The two dimensional model (2D model), which accounted for both radial and axial variations of temperature and concentrations under fully developed laminar flow.

Some findings from these models are presented in Appendix E, and the Fortran program listings for both models are given in Appendix F. Both models were used to determine reaction conditions which would limit the risk of an explosion. Selection of pilot plant reactor conditions was guided by the results from the mathematical analyses, and no explosive primary exotherm was encountered in the pilot plant. The mathematical models suggest that current reactor temperatures are only 15-20°C below the region of probable explosion, but their validity has not been determined experimentally. Reaction rate data used in the models were obtained from experiments in batch reactors (Appendix G).

3.6 Solvent Selection

Freon TF was selected as the basic solvent, primarily on the criterion of complete miscibility with N_2F_4, olefin, product, and reaction by-products. Other important requirements were non-flammability and stability in the presence of common chemicals, materials of construction, and N_2F_4 even at the elevated reaction temperature.

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[1] Rohm & Haas Company, Quarterly Progress Report on Chemical and Propellant Processing, No. P-64-3, August 6, 1964.

[2] Ibid, No. P-64-10, January 22, 1965.

[3] Rohm & Haas Company, Application of Flow Reactor Models to Process Simulation, No. S-54, October 9, 1964.

Since the olefins and products were soluble in most organic solvents, N_2F_4 solubility was a limiting factor. Incomplete solubility of N_2F_4 was unacceptable, because with even a small fraction of the gas present as a second phase the residence time in the reactor would be significantly reduced. The solubility of N_2F_4 was measured in five non-flammable solvents:[1,2,3] (1) Freon TF; (2) Freon MF; (3) chloroform; (4) carbon tetrachloride; and (5) methylene chloride. Of this group, Freon TF was about twice as good as the next best solvent, chloroform. The minimum 400 psig reactor pressure was established from N_2F_4 solubility measurements in the absence of the olefin (Appendix H); the effect of the olefin and/or product was not determined. All A-3 runs and the early TVOPA runs were made with pure Freon TF, but after initial trouble with reactor tube plugging, chloroform was added to the Freon TF for TVOPA synthesis to dissolve TVOP polymer (Section 3.7).

3.7 Operational Problems

Mechanical Problems

Although corrosion of the compressor parts by N_2F_4 was minor (Appendix I), considerable difficulties were encountered in obtaining and maintaining the necessary compressor capacity. Apparently, the formation of even a small amount of powdery corrosion product interfered with the check valve seating. The period between shut-downs forced by check valve leakage was substantially increased (from one to four months) by three modifications: (1) a sodium fluoride trap was added to absorb traces of hydrogen fluoride from the N_2F_4 feed; (2) bondable "Teflon" discs were cemented to the type 316 stainless steel valves to convert the seating to Teflon-to-metal from metal-to-metal; and (3) all the gas-wetted parts were thoroughly cleaned with a hot Triton®-water mixture each time check valve leakage occurred.

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[1]Rohm & Haas Company, Quarterly Progress Report on Physical Chemistry, P-62-25, April 1963.

[2]Ibid., No. P-63-25, February 7, 1964.

[3]Esso Research and Engineering Company, Quarterly Progress Report on Research on Advanced Solid Propellants, No. 61-3, September 19, 1961.

Reactor Plugging

Reactor plugging was sometimes encountered during the first batch immediately after change-over in adduct production. Apparently, solid by-products were gradually deposited on the reactor walls throughout the synthesis of both adducts, and the plugging was attributed to the dislodging of these solids by the change of reactant-product mixture. Because the pressure drop remained about constant through any series of batches with the same adduct, these solids were thought to be deposited as a thin film throughout the reactor tube. It was evident that the quantity of deposited solids was negligible compared to the quantity of adduct synthesized; 78 pounds of TVOPA was made without evidence of plugging.

A steam and water cleaning schedule was found to eliminate solids prior to interchange of adduct production (A-3 to TVOPA or vice versa). Before start-up acetone and then methylene chloride were used to remove all traces of water from the reactor coils.

Although TVOP polymerizes very slowly, enough polymer was formed under the N_2F_4 reaction conditions (100°C and a high concentration of NF_2 free radicals) to increase the pressure drop severely in a 0.118-inch I.D. tubular reactor during an operating period of an hour or more. Two process changes were required to eliminate this problem: (1) mixed solvent (4:1 ratio of Freon TF to chloroform) was chosen in which the TVOP polymer was at least partially soluble; and (2) the tube diameter was increased to 0.180-inch I.D.

3.8 Safety

About 3.5 pounds of N_2F_4 was lost from partial decomposition which occurred on one occasion with the opening of a main cylinder valve, and six explosive incidents were encountered during the two-year period the reactor was in operation. No personnel injury occurred, and equipment damage was minor. These incidents are discussed in Appendix J.

The synthesis of N_2F_4 adducts in the liquid phase reactor had a significant safety advantage, since the potentially explosive reactant-product mixture was heavily diluted with solvent. Thus, the 85% solvent dilution of the reactor effluent allowed non-remote handling of a desensitized product. Solvent dilution during reaction apparently eliminated explosion propagation through the liquid phase. All six explosions experienced during reactor operation were confined to short sections where the explosion initiated. In four instances the explosion occurred in the N_2F_4 mixing and absorption section during apparently trouble-free operation when the downstream section was filled with the reactants-product solution.

APPENDIX A

Properties of TVOPA and A-3

Physical properties for both A-3 and TVOPA are itemized in Table IV.

Table IV

Properties of TVOPA and A-3

	TVOPA	A-3
Appearance	clear liquid	clear liquid
Volatility	equivalent to triethylene glycol dinitrate	6.5 mm Hg at 50°C
Freezing point	< -30°C	< -30°C
Specific gravity	$1.54 \frac{28}{4}$	$1.43 \frac{20}{4}$
Viscosity, 30°C, cp	33	
Molecular weight	482	190
Weight % N_2F_4	64.7	54.6
Toxicity[a]	400-500	225

(a) LD_{50} in mg/kg of body wt. in acute oral tests on white, male Wistar rats; both compounds are classed as "highly toxic" on this basis.

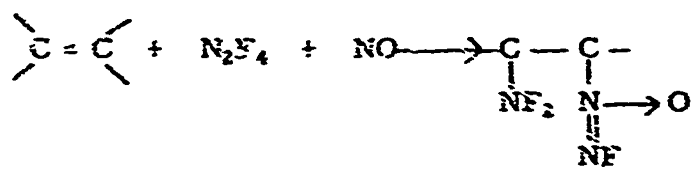
APPENDIX B

Raw Material Specifications

N_2F_4

Minimum N_2F_4 purity for TVOPA synthesis was set at 99 wt. % and for A-3 synthesis at 97 wt. %. For TVOPA synthesis nitric oxide content was limited to a maximum value of 0.3 wt. %.

Although the effect of impurities in N_2F_4 was not fully established, nitric oxide appeared to react preferentially during TVOPA synthesis to yield the fluoroazoxy impurity by the reaction shown in equation 4.



(4)

As shown in Fig. 3, the fluoroazoxy impurity in TVOPA increased about 3.5% (as the pentakis adduct) for each 1% NO in the N_2F_4 feed. A larger amount of NO could be tolerated in the A-3 synthesis, probably because of the fractionation of fluoroazoxy effected by subsequent reaction and purification steps in the NFPA synthesis.

Trivinoxypropane

Minimum assay of TVOP as determined by gas chromatography was set at 98%. Conversion calculations assumed 100% TVOP purity.

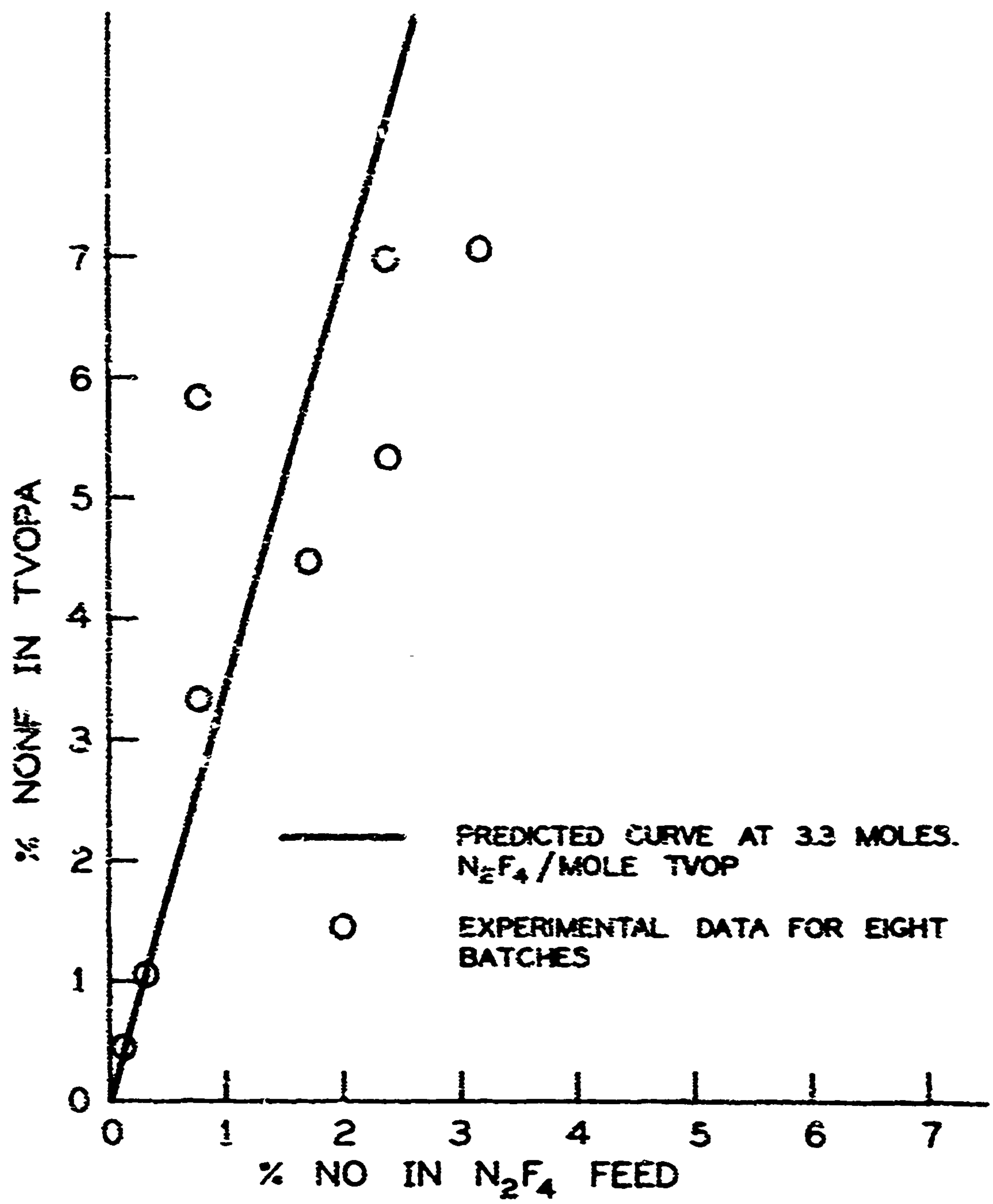


FIG. 3 FLUOROAZOXY CONTENT IN PRODUCT VERSUS NITRIC OXIDE CONTENT IN N_2F_4

APPENDIX C

Detailed Equipment Description

A flow sheet for the liquid phase flow reactor is shown in Fig. 2. The N_2F_4 compressor system, the two-stage tubular reactor, and the product work-up system were located for completely remote operation in a bay barricaded by 12-inch reinforced concrete walls. An 8-inch thick Plexiglas® sight port was provided for visual observation of the reactor bay from the control area, and the explosive limit on the bay was set at 5 lbs. Because N_2F_4 was condensable at the desired operating pressure, the entire reactor bay was thermostatted at 40°C (3.5°C above the critical temperature of N_2F_4)[1]. The N_2F_4 feed cylinders were located in an adjacent barricaded bay, and a second adjacent barricaded bay was used for product collection. The solvent-olefin feed tank and pump were located in the control area.

N_2F_4 Cylinder Manifold

The N_2F_4 cylinder manifold, shown in Fig. 4, served a dual purpose. First, it provided for ready replacement of N_2F_4 feed cylinders during any portion of the flow reactor operation; and second, it allowed recombination of nearly empty cylinders by compression into another gas cylinder. There were two independent cylinder manifolds containing one and three cylinders, respectively.

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[1]Rohm & Haas Company, Quarterly Progress Report on Air Force High Energy Solid Propellant Program, No. AF-8, February 9, 1961.

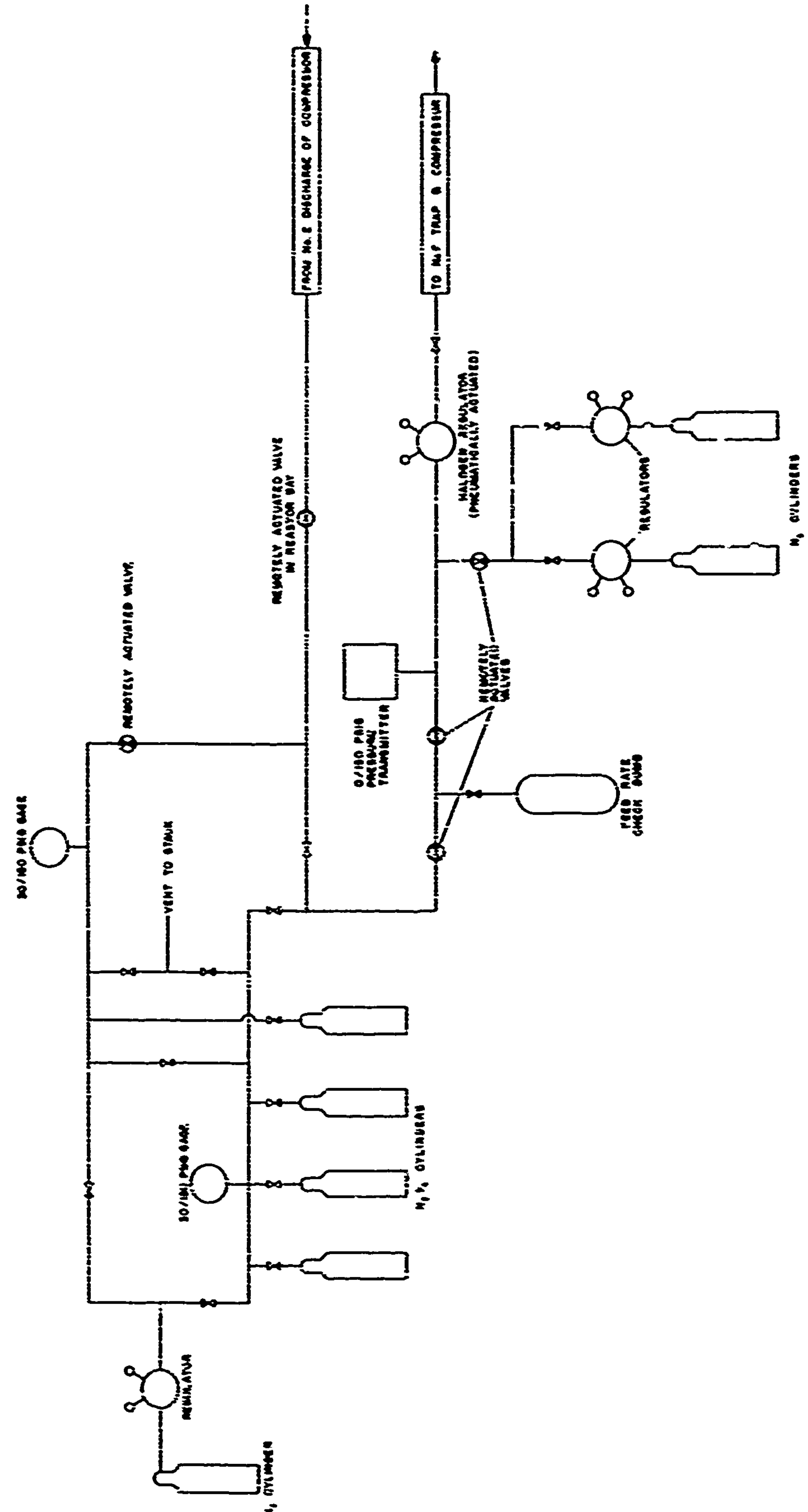

FIG. 4 N_2F_4 FEED MANIFOLD

The N_2F_4 was fed from a single cylinder, and about five hours was required to reduce the pressure from 130 psig to the 16 psig standard suction pressure of the compressor. Usually the three cylinders in a bank were emptied before any in that bank was replaced. Before cylinder removal and before the opening of a newly installed cylinder, the manifold was purged of air by five alternate fillings with 100 psig N_2 and ventings to atmosphere. The small amount of remaining atmospheric nitrogen was fed with the N_2F_4. The operating procedure for cylinder interchange is discussed in Appendix D.

Following an incident discussed in Appendix J, flame protection was provided during the opening of main N_2F_4 cylinder valves. Personnel were protected by a 12-inch reinforced concrete wall against which the cylinders were fixed. A two-foot long cable was inserted through the wall to open the valve. Care was taken to insure that the main cylinder valve was fully opened to take advantage of a second stem seal which was independent of the packing.

About 1/2 pound of N_2F_4 was recovered from each exhausted feed cylinder by recombination with the two-stage compressor. Typically, the compressor evacuated the 15-16 psig heels in the spent cylinders to 10-15 inches vacuum while discharging to as much as 110 psig. Mass spectral analyses confirmed a negligible change of N_2F_4 quality by this procedure. Six to nine cylinders could be emptied in a single day.

N_2F_4 Compressor System

A two stage, double diaphragm Lapp compressor having a nominal capacity of about 0.75 pounds of N_2F_4 per hour (15 psig to 500 psig) was used to compress the N_2F_4. The double diaphragm feature was chosen to avoid the mixing of N_2F_4 with the hydrocarbon oil if a leak should occur in the diaphragm, and the interdiaphragm space was filled with No. 3 Kel-F oil. However, no difficulty was encountered with diaphragm leakage.

A feed back control system was used to maintain the N_2F_4 feed rate to within ± 3.5% of the desired value. The feed rate was measured by a Fisher-Porter differential pressure transmitter (D/P cell) with an integrally mounted flow nozzle. The unit was continuously adjustable through a 0-20 to 0-200 inches of water range. A Minneapolis-Honeywell two-mode set-point recording controller (proportional plus automatic reset) was used to actuate the pneumatic stroke controller located on the first stage of the compressor. The D/P cell was attached to the suction side of the compressor. Suction pressure was controlled to 16 ± 0.5 psig with a Matheson Company halogen regulator. The regulator was modified for remote operation by substitution of pneumatic for mechanical actuation of the non-process side of the diaphragm. Continual adjustment of the pneumatic manual loader was required to maintain the suction pressure within ± 0.5 psig because pressure in the N_2F_4 supply cylinder dropped about 25 psi per hour during a run.

Periodic independent checks of the N_2F_4 feed rate confirmed the rate indicated by the D/P cell. A 2.5-liter cylinder was located downstream of the N_2F_4 feed cylinder, and the rate was checked by determining the pressure drop in this small cylinder over a period of four minutes. The small cylinder was immediately refilled (to feed cylinder pressure) by opening a connecting valve to the feed cylinder. This technique provided a rapid check on the D/P cell readout without seriously interfering with the absolute N_2F_4 feed rate.

Activated sodium fluoride was used in the HF trap. This was prepared by heating sodium bifluoride (1/4" x 1/4" pellets) overnight at 300°C while passing nitrogen through the bed to eliminate hydrogen fluoride.

Solvent and Olefin Feed

The solvent and olefin were premixed and metered with a 2300 cc/hr. capacity Lapp diaphragm pump. A glass wool filter was required to separate an oily material which otherwise interfered with the seating of

Hastelloy ball checks. Clear polyethylene tubing was used to connect the filter to the suction side of the metering pump, and this section was periodically checked to insure that the pump was not drawing air.

Mixing and Absorption

The N_2F_4 was mixed with the solvent-olefin in a cooled two-foot section of 1/4-inch I. D. tubing to control the heat of solution (4-6 kcal/mole) of N_2F_4 in the solvent.

Reactors

As shown in Fig. 5, each reactor chest was constructed from a schedule 40 6-inch water pipe, 30 inches long, vertically mounted, and insulated with about 2 inches of vermiculite. Each chest had provision for cooling with tap water, heating to 170°C with injected steam, and heating with hot water to about 95°C. A steam inlet was located at the bottom of the pipe, and the condensate overflow was from the top so that the tubular coils were totally immersed in the liquid bath. The tubular reactor was constructed by coiling 0.18 inch I. D. type 316 stainless steel tubing. The short section of tubing connecting the first and second stage was brine cooled.

Cooling and Depressurization

The effluent from the second stage of the reactor was cooled to less than 20°C before depressurization through two Grove back-pressure regulators which were mounted in series. The regulators controlled the reactor pressure by balancing nitrogen pressure on the upper side of the Teflon diaphragm against the pressure on the process side. As the process pressure exceeded the nitrogen balance pressure, the diaphragm opened, permitting process fluid to flow through an outlet nozzle. Because of the build up of a small amount of solid by-products on the outlet nozzle, sealing with one regulator was not always possible. Adequate sealing was obtained with the addition of the second regulator.

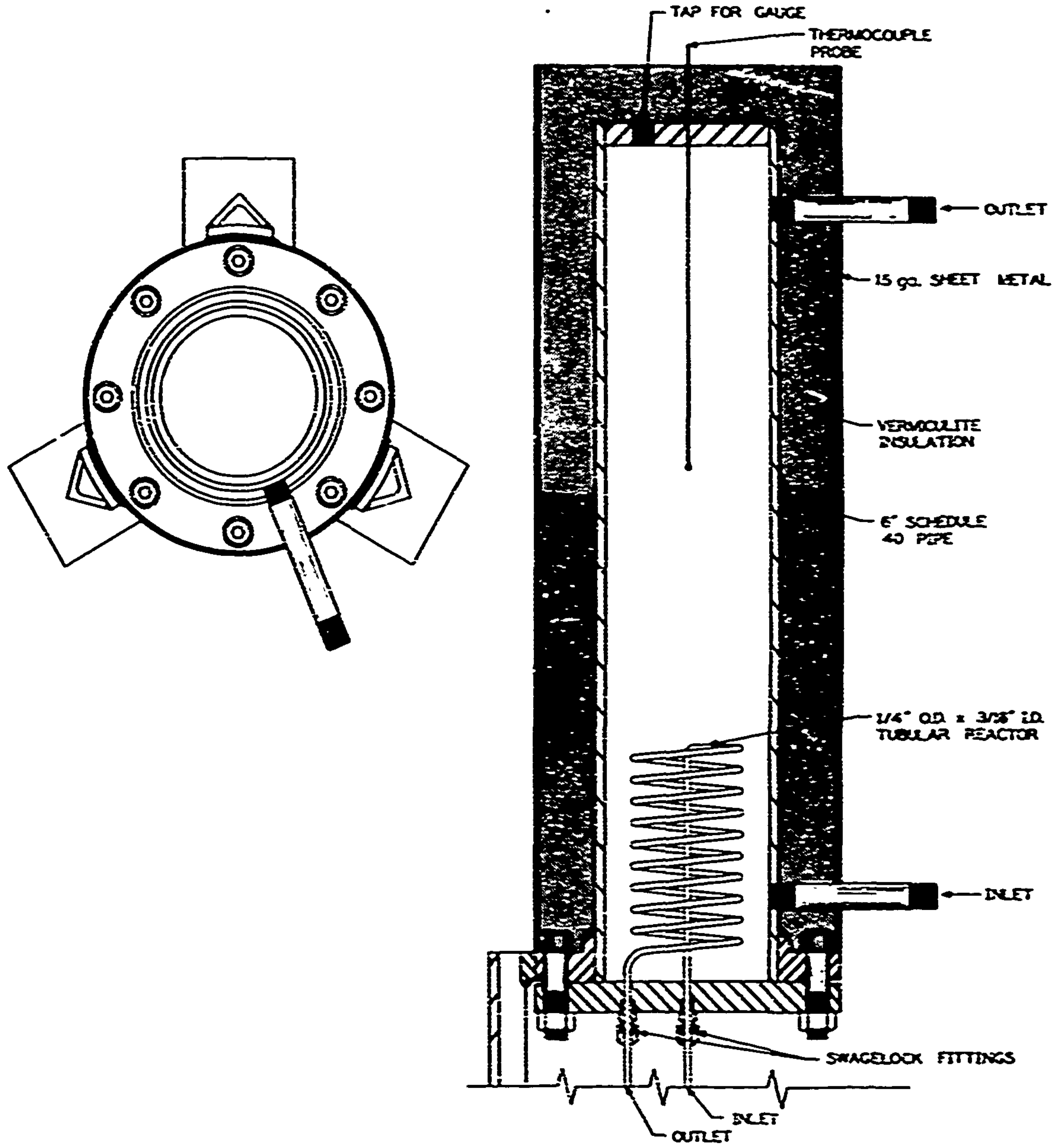

FIG. 5 TUBULAR REACTOR ARRANGEMENT IN REACTOR CHEST

N_2F_4 Desorption

Since both reactor effluents (TVOPA and A-3) readily wet 316 stainless steel, a wetted wall column (Fig. 6) was chosen for countercurrent desorption of the dissolved N_2F_4 in the depressurized effluent. The liquid was fed through the annulus and distributed to the column by overflowing around the inner perimeter. Nitrogen was fed to the bottom of the column at 1 liter per minute to dilute and sweep out the desorbed gas. The column temperature was about 40°C, which was the temperature of the thermostatted reaction bay. The column was 3 feet by 7/8-inch I.D. with a 1/8-inch annulus at the top formed by welding a 1 inch length of a larger, outer tube which extended 1/2-inch above the column.

Complete desorption of the N_2F_4 was confirmed by the absence of its characteristic odor in the effluent. Since there was concern that NF adducts containing absorbed N_2F_4 would deflagrate upon exposure to air, the product was air sparged (200 cc/min) in a hold-up vessel before collection in an adjacent bay. Because of the possibility of transmittal of such a deflagration, personnel were not allowed to enter the product collection bay while the air sparging operation was in progress. Entry was allowed while the hold-up vessel was temporarily used for the product collection, but only after the air was purged by nitrogen.

Liquid seals were used to prevent the nitrogen or air from flowing through the desorber drain line to the hold-up vessel or air flowing through the hold-up vessel drain line to the product collection bay. Two translucent polyethylene-U-tubes were installed so that a three-foot head differential was necessary for gas flow through the liquid lines. Repeated observation of the liquid levels confirmed that the seals were effective; typical liquid head differentials were in a range of 0 to 12 inches.

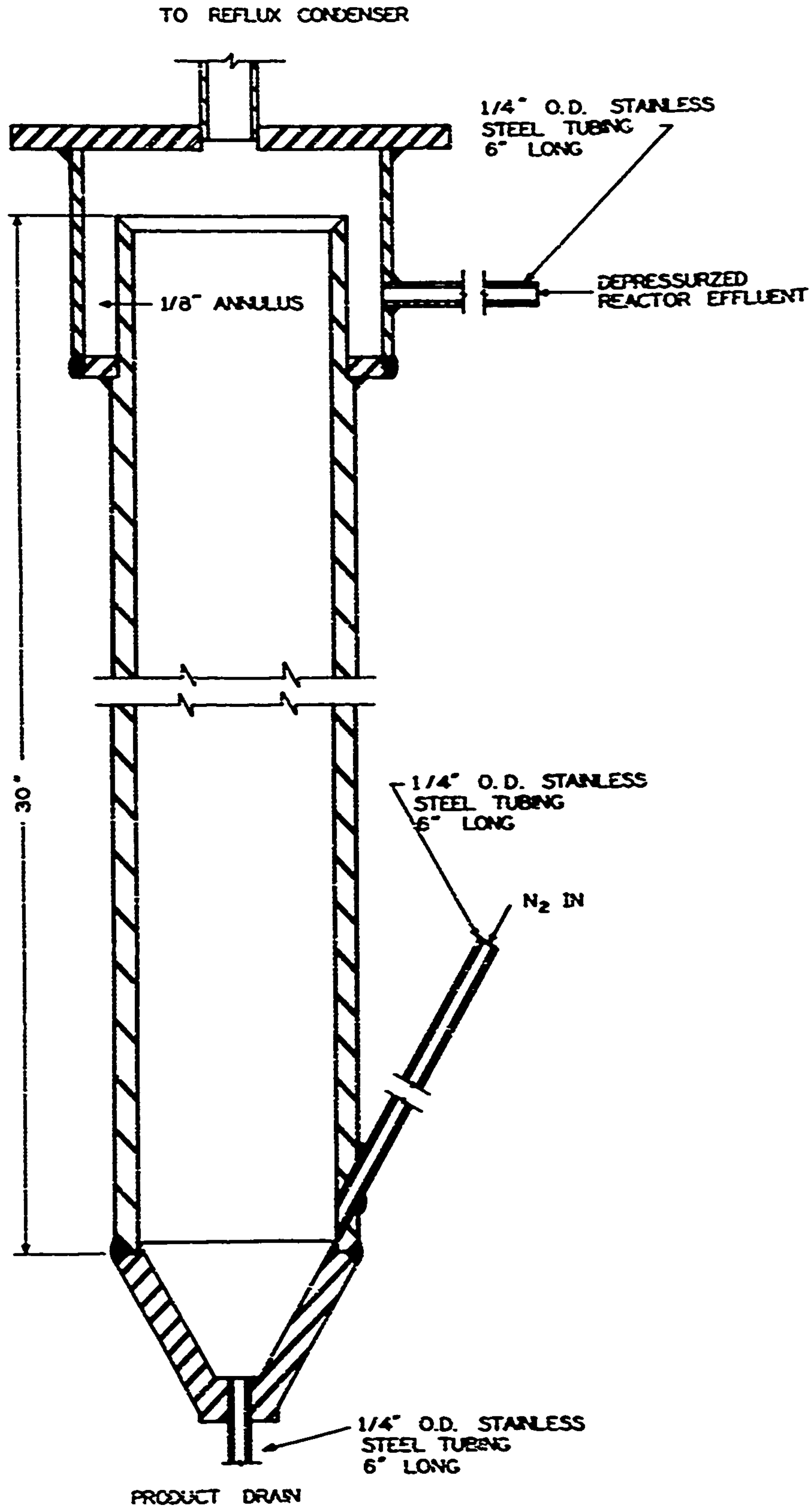

FIG. 6 WETTED WALL COLUMN

Venting of Unreacted N_2F_4

The unreacted N_2F_4 was vented directly to the atmosphere through a two inch aluminum stack at a 50 foot elevation. The nitrogen-N_2F_4 stream from the wetted wall column was diluted to about 30% with additional nitrogen, and upon entry to the stack, this mixture was further diluted with air so that the net concentration of original nitrogen-N_2F_4 mixture was reduced to less than 1% upon exhaustion to the atmosphere.

Materials of Construction

All pressurized process lines, with the exception of the N_2F_4 feed lines to the suction side of the compressor, all valves, and all process vessels were constructed of type 316 stainless steel. Hoke toggle valves with a Teflon tip were modified for remote actuation with an air cylinder. The N_2F_4 feed manifold was constructed of 1/4 inch copper tubing. Where possible, polyethylene tubing, either black or clear, was used for remote process lines operated at atmospheric pressure.

APPENDIX D

Standard Operating Procedure
for
High Pressure Liquid Phase Flow Reactor

General

The Section Safety Regulations are considered a part of this operating procedure and all applicable regulations must be observed.

Personal Protective Equipment

1. Safety goggles are required at all times except in the Bay H control area.
2. Safety goggles and rubber gloves are required while preparing solvent and olefin and while adding the mixture to the feed tank in Bay H.

Equipment Required

See Figures 2 and 4.

Process Description

The preparation of the product involves the liquid phase reaction of N_2F_4 dissolved in a suitable solvent with another reactant. The reaction is carried out in a jacketed tubular coil.

Safety Limits

The following limits must be observed, except for gas cylinders and 1/4-inch copper lines. Solvent used for dilution should not be considered explosive.

1.	Explosives in Reactor Bay:	1000 grams
2.	Explosives in Control Room:	zero
3.	Explosives in Product Collection Room:	10 pounds (never more than one day's run)
4.	Explosives in Cylinder Room:	zero
5.	Explosive charge per adduct container:	6 pounds

Safety Considerations

1. Once the door to the reaction area has been closed, never open it until shutdown procedure (for entry into the reactor bay) is followed. The door to the reaction area is not considered closed until the seven latches are secured.

2. Keep the door to the N_2F_4 cylinder storage bays closed except when it is necessary to take readings or move cylinders.

3. Handling of Product:

   a. i. Always carry product samples in a rubber boot.
      ii. Two-gallon polyethylene containers with handles may be hand carried.
      iii. Ten-gram samples are to be hand carried with the port directed away from the body.

   b. No more than six pounds of product will be added to any single storage container.

   c. Never transport the product or samples in the east corridor of Bldg. 7555.

   d. Open a product bottle which contains 35% or more concentrated adduct remotely if it has been stored longer than eight hours.

4. The west door to the Bay H control area should be closed at all times.

5. While handling solvent, etc. (in Bay H), be sure the exhaust fan is on.

Hazardous Properties of Chemical Compounds

1. N_2F_4 is considered highly toxic and can, even at low concentration, produce systemic injury if repeatedly inhaled. NEVER WORK OR REMAIN IN AN AREA WHERE THERE IS ANY PERCEPTIBLE ODOR OF N_2F_4. Personnel exposure must be limited to N_2F_4 stored at less than 150 psig in cylinders rated at greater than 2600 psig rupture pressure because of explosion hazard. Exceptions may be made by the supervisor.

2. Mixtures of N_2F_4 and air sometimes will initiate decomposition of the product, and the decomposition products may increase the product sensitivity to air. For this reason it is very important to leak test the flow reactor system before each run.

3. Treat N_2F_4 as if it were oxygen, that is, use oxygen fittings, valves, gages and regulators. NEVER ALLOW N_2F_4 TO COME IN CONTACT WITH GREASE OR SIMILAR HYDROCARBONS. SOME EXCEPTIONS WILL BE MADE WITH KEL-F GREASES, BUT ONLY AT THE DIRECTION OF THE SUPERVISOR. All process equipment must be degreased for oxygen usage.

4. No personnel should be in Bays E and F when N_2F_4 is introduced into the reactor feed lines. Before opening an N_2F_4 cylinder, be sure that the upstream remote valve to the system is closed.

5. The product is sensitive to shock and impact. For this reason it should be handled carefully. All bottles and vials containing this material must be clearly labeled as explosives.

6. Ingestion, inhalation, and contact of the product with the skin should be carefully avoided.

A. Preliminary Systems Check Out

1. All operating personnel should have completed at least two simulated emergency shutdowns.

2. If reactors are below 80°C, turn on heated water to both reactor stages and set water heater to 180°F (at 80°C set reactor temperature to that designated).

3. Check brine cooling system and turn on circulating pump.

4. Turn on air to the panel board and set regulator for instrument air controllers at 60 psig.

5. Set instrument air at 20 psig.

6. Close both N_2 back pressure valves on the panel board and N_2 feed to compressor, work-up vessel, wetted wall column, and dilution.

7. Turn on electricity to panel board.

8. Turn on lights in reaction area.

9. Turn on reaction area heater and set temperature at 40-42°C.

10. Turn on hot water to the Stage II compressor head and use hot water as necessary to maintain 40-50°C head temperature.

11. Turn on tap water to product cooling section.

12. Turn on all three nitrogen cylinders and replace if pressures are as follows: (vent air by filling and breaking at cylinder)

a.	Back Pressure N_2:	below 600 psig
b.	Emergency N_2:	below 1000 psig
c.	Sparge N_2:	below 1000 psig
d.	N_2F_4 feed cylinder:	as specified, and record analysis in log book

13. Do not replace any cylinder in the middle of a run; exceptions may be made by the supervisor.

14. Keep a cylinder log book for the N_2F_4 cylinders showing: (This is in addition to inventory requirements.)

    a. Date installed; Initial Pressure; Analysis

    b. Batch Numbers Used for

    c. Date Removed; Final Pressure

15. Turn on the exhaust fans in Bay F and Bay N.

16. Be sure glove for shutting down steam valves is "mounted" on panel board.

17. Close the drain valve on the vent trap.

B. Start-up

1. If for some reason the liquid level is below the drain valve in the Lapp pump, charge 100 ml of the chosen solvent (without olefin) and pump (full stroke) until the liquid level is just above the stopcock in the feed flask. Be sure the clear polyflow line connecting the filter to the liquid pump is filled with liquid.

2. Turn on sparge N_2 cylinder and set pressure regulator at 30 psig.

3. Close the valves to the wetted wall column and do not open until item No. 26.

4. If no overnight leak check has been applied: (no pressure drop should be allowed for 15 minute check or for overnight)

    a. Leak check at 30 psig for 15 minutes and include:

        (1) lines to main valve sparge N_2 cylinder
        (2) lines to main valve N_2F_4 cylinder
        (3) lines to mixing tee above compressor; do not turn on compressor to fill system
        (4) sparge N_2 system

    After venting the high pressure gage on the N_2 cylinder, observe the pressure recorder as well as the two discharge gages on the compressor.

    b. At the same time leak check the reactor system at the desired operating pressure to:

        (1) mixing tee
        (2) both the let-down vessel and the Grove valve, but not the column

c. At the same time leak check both N_2F_4 feed manifolds to 100 psig with N_2 or N_2F_4 pressure if above 15 psig; included are the remote N_2F_4 feed valve, vents, main cylinder valves, and No. 2 remote discharge valve. No pressure drop should be allowed even on an overnight check.

d. Vent the reactor system.

5. If air has been introduced to either the compressor or reactor systems, vent the reactor and compressor system and:

   a. At full stage I stroke, pump N_2 through the reactor system by filling at standard suction pressure and evacuating to 1-2 psig vacuum five times. All drain valves should be opened and a collection vessel should be under the work up vessel drain.

   b. Dispose of any liquid in explosive scrap and close drain valves.

6. Open the N_2 manifold valve on the panel board.

7. Turn on the N_2 to the column at 1.0 ℓ/min. (if different setting is used, record).

8. Turn on the N_2 to the dilution at 2.5 ℓ/min. (if different setting is used, record).

9. Turn on air to the work-up vessel at 0.2 ℓ/min. (if different setting is used, record).

9a. Turn on air to aluminum stack on the roof.

10. Be sure the door to the reaction area is closed and the red warning lights are on.

11. Adjust the pneumatic control valve.

12. Adjust both reactor stage temperatures as designated. While adjusting proceed to items 13-26.

13. Measure out the specified solvent and also measure out the specified quantity of olefin. Record the volumes on the batch card and measure the total volume before charging. Be sure these ingredients are completely mixed.

14. Set the solvent pump and charge the designated solvent-olefin mixture to the solvent feed tank.

15. Close the N_2F_4 feed valve and open the main N_2F_4 cylinder valve.

16. Adjust the halogen regulator to below 16 psig suction pressure.

17. Being sure the nitrogen feed valve is closed, open the N_2F_4 feed valve to the manifold.

18. Reset the halogen pressure regulator to the designated suction pressure.

19. Record null and full stroke compressor readings.

20. Apply pressure to the dome of the Grove valve.

21. If necessary, apply back-pressure to the system and close the back pressure valve.

22. Be sure collection jug is under work-up vessel outlet. Never remove jug without placing another 1000 cc collection vessel at the outlet.

23. Turn on the compressor adjusting the set point controller to the desired N_2F_4 feed rate.

24. When the downstream pressure reaches the back pressure, open the mixing tee valve.

25. If the compressor system did not contain N_2F_4, run for three minutes before going to item 26.

26. Turn on the solvent pump and start timer.

27. Open the column valves.

28. Wait 20 minutes and open the work-up vessel drain valve.

C. Operation

1. If it is necessary to go into the product collection bay:

   a. Close valve to work-up vessel.

   b. Turn off air.

   c. Turn on N_2 to work-up vessel at 0.5 ℓ/min., and after five minutes go to d.

   d. Enter product collection bay for a maximum period of 15 minutes.

   e. After leaving product collection bay tch to air flush at 0.2 ℓ/min.

   f. Open work-up vessel drain valve and co...ue collection.

2. Periodically check the N_2F_4 feed rate indicated by the D/P cel. This can be done by isolating the feed cylinder from the 2200 cc calibrated bomb as follows:

   a. Measure the pressure drop over a four minute interval.

   b. Find the feed rate from the graph, Figure 7.

   Adjust the D/P cell setting as required to maintain the designated N_2F_4 feed rate.

3. Record the items listed on the batch card at least every 45 minutes.

4. Observe the solvent rotameter, and if the flow should stop, shut down by the emergency shut down procedure.

5. If the polyethylene legs on the column and work-up vessel do not run full, notify supervisor, do not shut down, and do not enter Bay N.

6. If a new N_2F_4 feed cylinder is to be turned on during a run, do the following in the order listed. If trouble occurs (such as a stuck valve), go backwards from the step you are on to continue feeding from the near empty cylinder. If the problem is not readily solvable, shut the reactor down by the shut-down procedure and notify the supervisor.

   a. Close the remote N_2F_4 feed valve.

   b. Record the pressure and close the main cylinder valve on the nearly empty cylinder.

   c. Open the main cylinder valve on the full cylinder.

   d. Record the cylinder pressure.

   e. Set the manual valves to feed through the remote N_2F_4 feed valve.

   f. Being sure there are no personnel in Bays E or F, remotely open the N_2F_4 feed valve.

7. Be sure the clear polyflow tube between the filter and the liquid pump is filled with liquid.

D. Shutdown Procedure

1. With the solvent pump running, quickly collect the excess solvent-olefin mixture in the designated receiver. Drain to just above the stopcock and add (exactly) 1800 ml solvent mixture (use 1000 ml for overnight shutdown where same adduct is to be made the next day). Record time at completion. Wait 2 minutes and then proceed to item 2.

2. Close the N_2F_4 feed valves and all main N_2F_4 cylinder valves.

3. At 8 psig suction close the mixing tee valve and turn off compressor.

4. After feeding at least 300 ml solvent, open the pump to full stroke.

5. Turn off the solvent pump when the liquid level in the glass feed tank is about 3/4-in. above the stopcock and close the column feed valve and drain valve to let down vessel.

6. Turn off the N_2 to the dome and depressurize by venting through the pneumatic valve and then close pneumatic valve and repressurize.

7. If this is an overnight shut down, apply the leak check as in the start-up instructions. Record each pressure and temperature for each bay.

8. Be sure the work-up vessel has been emptied of liquid. Do this by increasing the N_2 dilution to 15 l/min. for at least 3 minutes.

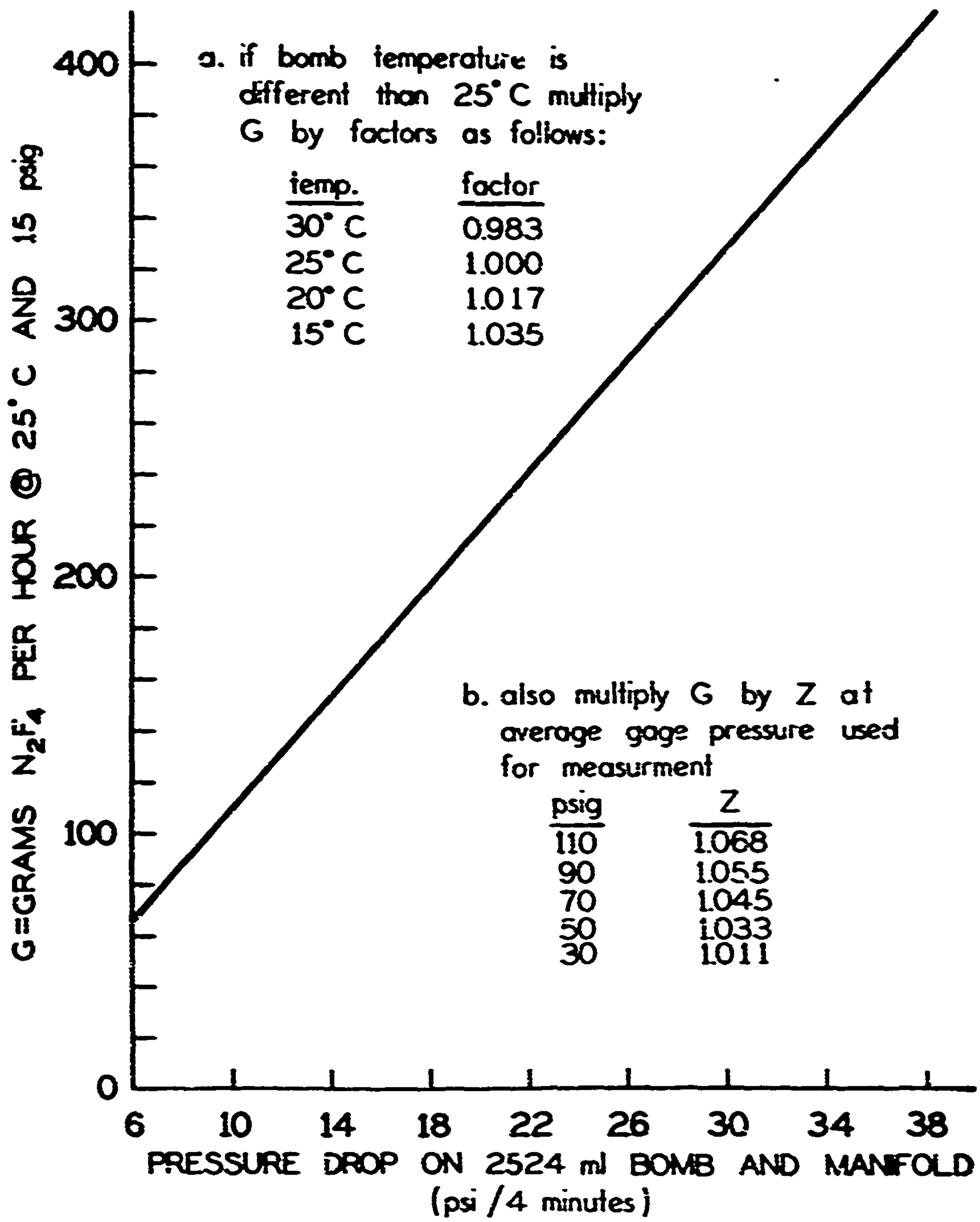

FIG. 7 N_2F_4 FEED RATE CALIBRATION GRAPH

9. If shut down is for entry into the reaction bay, very slowly over a period of at least 15 minutes vent the reactor by opening the Grove valve and the column valves and the drain valve on the work-up vessel. Clean the N_2F_4 feed lines by the following technique (be sure there is a collection vessel under the work-up vessel):
   a. Open the N_2 feed valve to pressurize the compressor system and turn on the compressor.
   b. After about 15 seconds, close the N_2 feed valve and open the mixing tee valve.
   c. When the suction pressure reaches 1-2 psig repeat a and b five times and then pressurize the suction lines to at least 5 psig.
   d. Close mixing tee valve and shut off compressor.
10. After the solvent is collected, turn off the following:
   a. Bay lights and warning lights if the reactor bay can be entered.
   b. All main N_2F_4 cylinder valves.
   c. Compressor.
   d. Sparge N_2 cylinder.
   e. Temperature recorder.
   f. Air to stack and work-up vessel.

   Also:

   g. Open drain valve on the vent trap.
   h. Do not turn off room heater or cooling system including pump.
11. Store the unused solvent-olefin mixture and label as follows:
   a. Gross weight.
   b. Tare weight.
   c. Net weight (note on batch card).
   d. Nominal concentration of each component.
   e. Date.
   f. Batch No.

E. Emergency Shut Down Procedure

1. If any unusual difficulty occurs, follow this procedure immediately in the sequence listed.
2. Turn off N_2F_4 feed valve to compressor and close mixing tee valve.
3. Close work up vessel drain valve.

4. Cool stage II with tap water to the stage I temperature. While waiting, turn on emergency alarm. Only one operator is to remain in Bay H to complete procedure through Item 10.
5. Cool stage I with tap water, and when both reactors are less than 40°C, proceed.
6. Turn off solvent pump.
7. Turn on N_2 feed to compressor and open mixing tee valve.
8. Set first stage compressor stroke control to 15 psig.
9. Turn pneumatic bleed valve to 15 psig and close N_2 valve to the dome.
10. Consult supervisor. (No watch is necessary after completion of item 8.)

F. Changing N_2F_4 Cylinder

1. Isolate manifold where cylinder is to be added.
2. Close all main N_2F_4 cylinder valves in this manifold.
3. Pressurize the manifold to 100 psig with N_2 and vent. Do this at least five times.
4. Remove the N_2F_4 cylinder.
5. Replace with a new cylinder.
6. Fill the system to 100 psig with N_2 and vent five times.

G. Routine Maintenance (once per month or oftener as required)

1. Each item should be tagged with the date and service received.
2. Grease bearings on compressor motor.
3. Check gear box level on compressor motor.
4. Inspect oil in each compressor stage and, if necessary, change.
5. Inspect oil in solvent pump and, if necessary, change.
6. Sparingly grease all air cylinder rods.
7. Drain air filter and, if necessary, replace.
8. Add make up brine to the cooling system.

H. Interchange of Product

1. If the next batch is to be a different adduct, follow this procedure after following the procedure for entry into the reactor bay.
2. Set the reactor coils for atmospheric pressure operation and flush the brine from the cooling lines with air.
3. Heat both reactors to 103°C with steam.
4. Pump 1000 ml of water through the unit and collect in the product collection bay.
5. Cool the reactors to less than 30°C.
6. Pump 500 cc water.
7. Pump 500 cc acetone.
8. Pump 1500 cc methylene chloride.
9. Dump the solvent water mixture in explosive scrap.
10. The unit is now ready to run on a different adduct.

APPENDIX E

Exotherm Characterization

The addition of N_2F_4 to olefins was exothermic by about 35 kcal/gm mole of N_2F_4 added. For example, 105 kcal were liberated by the addition of 3 moles of N_2F_4 to one mole of TVOP. Exotherm control appeared necessary to avoid explosive incidents. Two mathematical models were developed to characterize the reaction exotherm based upon laboratory kinetic studies. These models were:

(1) The bulk model which assumed a slug flow profile with concentrations and temperatures varying only along the tubular axis.

(2) The two-dimensional model (2D) which included radial diffusion of temperature and both reactants under fully developed laminar flow.

The maximum temperature limit was based upon differential thermal analysis of TVOPA thermal decomposition. Since the DTA indicated that TVOPA began to decompose at above 150°C, operating conditions were chosen never to exceed a 140°C reactant temperature. The operating bath temperature was set at 10°C below the temperature where the exotherm caused a 140°C reactant temperature. This criterion provided an adequate safety factor to allow for expected process deviations such as ± 2°C variation in bath temperatures, ± 3.5% variation in N_2F_4 feed rate, and ± 1% variation in the solvent + olefin feed rate.

Computer studies based on the mathematical models indicated that current operating conditions were about optimum for the temperature requirements outlined above. Three commercially available tube diameters - 0.118 inch I.D., 0.180 inch I.D. and 0.305 inch I.D. - were compared. Lower bath temperatures were required with increased tube diameters because of the decreased heat transfer surface to volume ratio. Consequently, the quantity in process was found to decrease with decreasing tube diameter. Since the

0.118 I.D. was easily plugged during TVOPA synthesis, the 0.180 inch I.D. was selected for the tubular reactor.

A minimum TVOP conversion of 95% was chosen to minimize purification requirements. Excess N_2F_4 was required to obtain reasonable coil lengths at this conversion. Since the expected gas and liquid feed rate variations could vary the N_2F_4 concentration by ± 5%, a 10% excess appeared to be an acceptable compromise of reactor length and N_2F_4 usage. Further increases were not justified because of the high cost of N_2F_4 compared to the savings in reactor length. For example, only a 12% reduction in reactor length was calculated for 30% excess N_2F_4.

The N_2F_4 concentration of 0.004 grams N_2F_4/cc solvent was found to minimize reactor length for a reactor with two to five stages. About 40% reduction in total coil length was calculated for a three stage reactor compared to a two stage reactor. However, the reduction depended upon operation of the last stage at 125° C, and the effect of a 125° C bath temperature on TVOPA product quality has not been determined.

Results from both the 2D model and the bulk model were considered in selecting the operating conditions for the pilot plant reactor. The centerline temperature from the 2D model was used and compared with the bulk temperature from the bulk model. The maximum permissible first stage bath temperature obtained from the bulk model was 85° C, or about 5° C below the 90° C obtained from the 2D model. Both models indicated a runaway reaction at 12° C above their respective bath temperatures. For other stages where at least 30% of the TVOP was already converted, there was not a significant difference between the maximum permissible bath temperatures calculated from the two models. Because the limit was on the centerline temperature with the 2D model, its average (bulk) temperature was less than that for the bulk model. Consequently, the 2D model required a longer reactor tube for equivalent conversion. No attempt was made to determine the validity of either model and reaction conditions were selected conservatively. Bath

temperatures were based on the bulk model and reactor length was chosen from the 2D model. A comparison of the exotherm and conversion predictions is shown in Fig. 7.

The interstage addition of TVOP was investigated as a technique of reducing reactor length for a three stage reactor. The N_2F_4 was added to the solvent containing some TVOP, and additional TVOP was added to the second stage to limit the excess N_2F_4 to 10%. Computer results for these conditions showed a reduction of about 10% in the total tube length at a final stage temperature of 125°C. This small decrease was not sufficient to justify the addition of a second liquid pump for the TVOP.

APPENDIX F

Listing of FORTRAN Programs for Mathematical Models

The FORTRAN listings of the computer programs used in making the calculations discussed in this report are provided on the following pages, along with printouts of a typical problem. Preceding the FORTRAN listings is an explanation of the input data required by the program. The format used to read the input data can be obtained from the FORTRAN listings.

2D Flow Model Computer Program

Input Data for 2D Flow Model Computer Program

Fortran Symbol	Meaning	Units for 0.18" I.D. Tubing	
J	No. of pairs of points describing bath temperature		
INPT	1. 2D print out showing all radial points 2. 2D print out showing only centerline points and bulk conversion		
NX	number of radial increments	10	
IBTA	number of DELX increments between printout (a)	80 100	 for CAPR of 0.100
FK	thermal conductivity of reacting solution	0.[illegible]3	BTU/hr-ft-°F
DFT	diffusion coefficient of reacting species M	0.00009	ft²/hr
DFN	diffusion coefficient of reacting species N	0.00015	ft²/hr
A	constant in reaction rate expression	0.321 exp + 18	cc soln/gm mole
B	constant in reaction rate expression	0.1995 exp + 5	°R
TAR	constant to convert to absolute temperature (TAR = 460)		°R
AA	exponent for conc. CN in reaction rate expression	1	
BB	exponent for conc. CM in reaction rate expression	1	
TI0	initial temperature of solution entering reactor	-20	°C
DELX	spatial increments in axial direction	0.0125 0.0100	ft. for CAPR of 0.100

Fortran Symbol	Meaning	Units for 0.18" I.D. Tubing	
DELR	spatial increments in radial direction	0.00075	ft.
RR	radius of tube	0.0075	ft.
XMAX	maximum length in reactor (to stop comp.)	______	ft.
HO	heat transfer coefficient (tubewall to bath)	200	BTU/hr-ft^2-°F
PROB	problem identification number	______	
Y	TVOP feed rate	100	gms. TYOP/hr.
CON	fraction TVOP converted on input	______	%/100
CAPR	N_2F_4 concentration at 0% TVOP conversion	______	gms. N_2F_4/cc solvent
LCR	mole ratio at 0% TVOP conversion	______	$\frac{\text{moles } N_2F_4}{\text{moles TYOPA}}$
XX1	distance to first environment temperature point	______	ft.
TS1	temperature at first environment temperature point	______	°C
XX2	distance to second environment temperature point	______	ft.
TS2	temperature at second environment temperature point	______	°C
XXJ	distance to jth environment temperature point	______	ft.
TSJ	temperature at jth environment temperature point	______	°C

(a) Chosen to satisfy inequality as outlined in Rohm & Haas Company, Report No. S-56, Application of Flow Reactor Models to Process Simulation, October 9, 1964.

FORTRAN Listing

2D Model of Flow Reactor

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MAIN                                                     07/07/65                        PAGE 1
     EXTERNAL FORMULA NUMBER   -   SOURCE STATEMENT   -   INTERNAL FORMULA NUMBER(S)

C XI000S-A LAMINAR FLOW MODEL, LIQUID PHASE FLOW REACTOR FOR WILLOUGHBY
C     LIQUID PHASE FLOW REACTOR, TWO-DIMENSIONAL MODEL, PROGRAM II
C     DON WILLOUGHBY, ROHM AND HAAS COMPANY
      DIMENSION T1(50),T2(50),CT1(50),CT2(50),CX1(50),CX2(50),CP1(50),
     1CP2(50),XX(100),TS(100),DT(50),UR(50),C(50),DELQ(50),Q2(50),
     2CB1(50),CD1(50),CF1(50),CB2(50),CD2(50),CF2(50),CB3(50),CD3(50),
     3CF3(50),CB4(50),CD4(50),CF4(50)
   10 FORMAT (5E14.7)
   11 FORMAT (4I5)
   12 FORMAT (64H1 TWO-DIMENSIONAL MODEL OF LIQUID PHASE FLOW REACTOR,
     1PROGRAM 2/)
   13 FORMAT (16H PROBLEM NUMBER  E14.7/)
   14 FORMAT (24H EQUATIONS UNSTABLE,STOP)
   15 FORMAT (7H TIME = E14.7,16H      DISTANCE =E14.7,30H     ENVIRON
     1MENT TEMPERATURE =E14.7)
   17 FORMAT (29H TEMPERATURES FOLLOW. TBULK= E14.7)
   18 FORMAT (8(2XE14.7))
   19 FORMAT (35H CT CONCENTRATIONS FOLLOW. CTBULK = E14.7)
   20 FORMAT (35H CX CONCENTRATIONS FOLLOW. CXBULK = E14.7)
   21 FORMAT (35H CP CONCENTRATIONS FOLLOW. CPBULK = E14.7)
   22 FORMAT (5H      C=E14.7,8H     FK=E14.7,8H   DEN=E14.7,8H    EFT=
     1E14.7,8H   [illegible]=E14.7)
   23 FORMAT (5H      A=E14.7,8H     B=E14.7,8H    TAR=E14.7,8H     AB=
     1E14.7,8H   BS=E14.7)
   24 FORMAT (5H   DELH=E14.7,8H   CTO=E14.7,8H   CXO=E14.7,8H    CPO=
     1E14.7,8H   TIO=E14.7)
   25 FORMAT (5H   DELX=E14.7,8H   DELR=E14.7,8H   RR=E14.7,8H    XMX=
     1E14.7,8H   [illegible]=E14.7)
   26     FORMAT(18H   VEL=E14.7,8H      Y=E14.7,8H   CON=E14.7,8H  CAPR=E
     1E14.7,8H   [illegible]=E14.7)
   27 FORMAT (5H       J=I5,5H   INPT=I5,8H     NK=I5,5H    ISTA=I5)
   28 FORMAT (25H    XX VALUES             TS VALUES)
   29 FORMAT (2E14.7)
   30     READ (5,11)J,INPT,NK,ISTS                                   .1   .2   .3   .4   .5   .6
   31     READ (5,10)[illegible]                                      .7   .8   .9
     1,CON,CAPR,SMALR
      IFLAG=1                                                        .10
   32 READ (5,10) (XX(I),TS(I),I=1,J)                                 .11  .12  .13  .14  .15
      PART=1. + CAPR/1.25 + [illegible]                               .16
      CTO=(1.-CON)*((CAPR/(104.*SMALR))/[illegible])                  .17
      CXO=[illegible]                                                 .18
      CPO=(CON*CTO)/(1.-CON)                                          .19
      VEL=(3.531E-05/536.0)[illegible]                                .20
   50     CRAT = CTO / (1. - CON)                                     .21
      CRAT2=CXO/(1. - 3.*CON/SMALR)                                   .22
      Y1=83.1*CRAT2                                                   .23
   51     [illegible]                                                 .24
      Y5=1.0-Y1-Y2                                                    .25
   53     DEN=(104.0*CRAT2+170.0*CRAT+1.52*Y5)*62.4                   .26
   54 DELH=[illegible]                                                .27
   55 B3=[illegible]                                                  .28
   56 B4=[illegible]                                                  .29
   57     [illegible]                                                 .30
   58     Y2=CRAT2/AX                                                 .31
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                 MAIN                                                   07/07/65                                  PAGE  2
        EXTERNAL FORMULA NUMBER   -   SOURCE STATEMENT   -   INTERNAL FORMULA NUMBER(S)

    49 Y2=X2/AX                                                     55    .32
    50 Y3=X3/AX                                                     56    .33
    51 Y4=X4/AX                                                     57    .34
    52 C=Y1*0.29+Y2*0.46+0.213*Y3+0.234*Y4                          58    .35
    53 WRITE (6,12)                                                 59    .36    .37
    54 WRITE (6,13) PROB                                            60    .38    .39    .40
    55 WRITE (6,22) C,FK,DEN,CFT,CFM                                61    .41    .42    .43
    56 WRITE (6,23) A,B,TAX,AA,BB                                   62    .44    .45    .46
    57 WRITE (6,24) DELH,CIO,CNO,CPO,TIO                            63    .47    .48    .49
       TIO=1.8 *TIO + 32.                                           64    .50
    58 WRITE (6,25) DELX,DELR,RR,RRI,HO                             65    .51    .52    .53
39     WRITE (6,26)VEL,Y,CON,CAPM,SMALR                             66    .54    .55    .56
    60 WRITE (6,27) J,INPT,NK,IBTA                                  67    .57    .58    .59
    61 WRITE (6,28)                                                 68    .60    .61
    62 WRITE (6,29) (XX(I),TS(I),I=1,J)                             69
C      CONVERT TS TO DEGREES F                                      70    .62    .63    .64    .65    .66
       DO 1000 I=1,J                                                71    .67
1000   TS(I)=1.8 *TS(I) + 32.                                       72
C      PRELIMINARY CALCULATIONS FOLLOW                              73    .68    .69
    70 DELT=DELX/VEL                                                74    .70
    71 IMALL=NK+1                                                   75    .71
    72 AVEL=RR*RR*VEL                                               76    .72
    73 R=0.0                                                        77    .73
    74 DO 85 I=1,IMALL                                              78    .74
    75 CT(I)=CTO                                                    79    .75
    77 CN(I)=CNO                                                    80    .76
    79 CP(I)=CPO                                                    81    .77
    81 T(I)=TIO                                                     82    .78
    83 DT(I)=DELX/(2.0*VEL*(1.-R/RR*R/RR))                          83    .79
    84 R=R+DELR                                                     84    .80
    85 CONTINUE                                                     85    .81    .82
    86 ICNT=IBTA                                                    86    .83
    87 ALPHA=FK/DEN/C                                               87    .84
    88 IF(ALPHA-CFM) 89,91,91                                       88    .85
    89 DF=CFM                                                       89    .86
    90 GO TO 92                                                     90    .87
    91 DF=ALPHA                                                     91    .88
    92 IF(DF-CFT) 93,94,94                                          92    .89
    93 DF=CFT                                                       93    .90
    94 CONTINUE                                                     94    .91
    95 FA=DELR/RR                                                   95    .92
    96 FP=DELX/DELA                                                 96    .93
    97 CON1=2.0*FA*FA*FA*FA*FA                                      97    .94
    98 CON2=FA/2.0                                                  98    .95
    99 IF(CON1-CON2) 100,102,102                                    99    .96
   100 CON3=CON1                                                   100    .97
   101 GO TO 103                                                   101    .98
   102 CON3=CON2                                                   102    .99
   103 CONTINUE                                                    103    .100
   104 CON4=VEL*RR/DF*CON3                                         104    .101
   105 IF(FP-CON4) 108,106,106                                     105    .102
   106 WRITE (6,14)                                                106    .103   .104
   107 GO TO 30                                                    107    .105
   108 CONTINUE                                                    108    .106
   110 X=0.0                                                       109    .107
   111 TT=0.0                                                      110    .108
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                MAIN                                             03/07/65                PAGE  3
---    EXTERNAL FORMULA NUMBER   -   SOURCE STATEMENT   -   INTERNAL FORMULA NUMBER(S)

 112 J=1                                                          111    .109
 113 XM=(TS(2)-TS(1))/(XX(2)-XX(1))                               112    .110
 114 UR(1)=VEL*(1.0-DELR/RR*DELR/RR/18.0)*DELR/2.0*DELR           113    .111
 115 R=DELR                                                       114    .112
 116 DO 118 I=2,NX                                                115    .113
 117 UR(I)=4.0*VEL*(1.0-R/RR*R/RR)*R*DELR                         116    .114
 118 R=R+DELR                                                     117    .115   .116
 119 UR(IWALL)=2.0*VEL*(1.0-(RR-DELR/4.0)**2.0/RR/RR)*(RR-DELR/4.0)*   118
    1DELR                                                         119    .117
 120 TI(IWALL)=TS(1)                                              120    .118
 121 CA=2.0*VEL/DELR                                              121    .119
 122 CAA1=4.0/DELR/DELR/CA                                        122    .120
 123 CA1=ALPHA*CAA1                                               123    .121
 124 CA2=1.-CA1                                                   124    .122
 125 CA3=DELR/C/CA                                                125    .123
 126 CC1=DFN*CAA1                                                 126    .124
 127 CC2=1.-CC1                                                   127    .125
 128 CC3=1.0/CA                                                   128    .126
 129 CE1=DFT*CAA1                                                 129    .127
 130 CE2=1.-CE1                                                   130    .128
 131 CE3=1.0/3.0/CA                                               131    .129
 132 R=DELR                                                       132    .130
 133 DO 149 K=2,NX                                                133    .131
 134 CB=2.0*VEL/DELR*(1.-R/RR*R/RR)                               134    .132
 135 CB11=(1.0/DELR/DELR+0.5/R/DELR)/CB                           135    .133
 136 CB1(K)=ALPHA*CB11                                            136    .134
 137 CD1(K)=DFN*CB11                                              137    .135
 138 CF1(K)=DFT*CB11                                              138    .136
 139 CB22=(1.0/DELR/DELR-0.5/R/DELR)/CB                           139    .137
 140 CB2(K)=ALPHA*CB22                                            140    .138
 141 CD2(K)=DFN*CB22                                              141    .139
 142 CF2(K)=DFT*CB22                                              142    .140
 143 CB3(K)=(CB-2.0*ALPHA/DELR/DELR)/CB                           143    .141
 144 CD3(K)=(CB-2.0*DFN/DELR/DELR)/CB                             144    .142
 145 CF3(K)=(CB-2.0*DFT/DELR/DELR)/CB                             145    .143
 146 CB4(K)=DELR/C/CB                                             146    .144
 147 CD4(K)=1.0/CB                                                147    .145
 148 CF4(K)=CD4(K)/3.0                                            148    .146
 149 R=R+DELR                                                     149
C       INLET TO MAIN CALCULATION LOOP                            150    .147   .148
 300 CONTINUE                                                     151    .149
 301 IF(XX(J+1)-X) 302,305,305                                    152    .150
 302 J=J+1                                                        153    .151
 303 XM=(TS(J+1)-TS(J))/(XX(J+1)-XX(J))                           154    .152
 304 GO TO 301                                                    155    .153
 305 TE=TS(J+1)-XM*(XX(J+1)-X)                                    156    .154
 500 DO 508 K=1,NX                                                157    .155
 501 Q(K)=-A*EXP(-B/(TI(K)+TAA))*CN1(K)**AA*CT(K)**BB             158    .156
 502 DELC(K)=DT*Q(K)                                              159    .157
 503 Q2(K)=CN1(K)+DELC(K)                                         160    .158
 504 IF(Q2(K)) 505,506,506                                        161    .159
 505 Q2(K)=0.0                                                    162    .160
 506 DELC(K)=-CN1(K)                                              163    .161
 507 Q(K)=DELC(K)/DT(K)                                           164    .162
 508 CONTINUE                                                     165    .163   .164
 510 CN2(1)=CC1*CN1(2)+CC2*CN1(1)+CC3*Q(1)                        166    .165
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      MAIN                                                    07/07/65                          PAGE  4
   EXTERNAL FORMULA NUMBER   -   SOURCE STATEMENT   -   INTERNAL FORMULA NUMBER(S)

511 IF(CN2(1)) 512,515,515                                                   167    .166
512 Q(1)=-(CC1*CN1(2)+CC2*CN1(1))/CC3                                        168    .167
513 DELC(1)=Q(1)*DT(1)                                                       169    .168
514 CN2(1)=0.0                                                               170    .169
515 CT2(1)=CE1*CT1(2)+CE2*CT1(1)+CE3*Q(1)                                    171    .170
516 IF(CT2(1)) 517,521,521                                                   172    .171
517 Q(1)=-(CE1*CT1(2)+CE2*CT1(1))/CE3                                        173    .172
518 DELC(1)=Q(1)*DT(1)                                                       174    .173
519 CT2(1)=0.0                                                               175    .174
520 CN2(1)=CC1*CN1(2)+CC2*CN1(1)+CC3*Q(1)                                    176    .175
521 CP2(1)=CP1(1)-DELC(1)/3.0                                                177    .176
522 T2(1)=CA1*T1(2)+CA2*T1(1)-CA3*Q(1)                                       178    .177
530 DO 544 K=2,NX                                                            179    .178
531 CN2(K)=CD1(K)*CN1(K+1)+CD2(K)*CN1(K-1)+CD3(K)*CN1(K)+CD4(K)*Q(K)         180    .179
532 IF(CN2(K)) 533,535,535                                                   181    .180
533 Q(K)=-(CD1(K)*CN1(K+1)+CD2(K)*CN1(K-1)+CD3(K)*CN1(K))/CD4(K)             182    .181
534 DELC(K)=Q(K)*DT(K)                                                       183    .182
535 CN2(K)=0.0                                                               184    .183
536 CT2(K)=CF1(K)*CT1(K+1)+CF2(K)*CT1(K-1)+CF3(K)*CT1(K)+CF4(K)*Q(K)         185    .184
537 IF(CT2(K)) 538,542,542                                                   186    .185
538 Q(K)=-(CF1(K)*CT1(K+1)+CF2(K)*CT1(K-1)+CF3(K)*CT1(K))/CF4(K)             187    .186
539 DELC(K)=Q(K)*DT(K)                                                       188    .187
540 CT2(K)=0.0                                                               189    .188
541 CN2(K)=CD1(K)*CN1(K+1)+CD2(K)*CN1(K-1)+CD3(K)*CN1(K)+CD4(K)*Q(K)         190    .189
542 CP2(K)=CP1(K)-DELC(K)/3.0                                                191    .190
543 T2(K)=CB1(K)*T1(K+1)+CB2(K)*T1(K-1)+CB3(K)*T1(K)-CB4(K)*Q(K)             192    .191
544 CONTINUE                                                                 193    .192  .193
545 T2(IWALL)=TE+FK/HC/DELR*(T1(IWALL-1)-T1(IWALL))                          194    .194
546 CN2(IWALL)=CN2(NX)                                                       195    .195
547 CP2(IWALL)=CP2(NX)                                                       196    .196
548 CT2(IWALL)=CT2(NX)                                                       197    .197
550 IF(ICNT-ISTA) 604,555,604                                                198    .198
555 BLKT=0.0                                                                 199    .199
556 BKCN=0.0                                                                 200    .200
557 BKCT=0.0                                                                 201    .201
558 BKCP=0.0                                                                 202    .202
559 DO 564 I=2,NX                                                            203    .203
560 BLKT=BLKT+UR(I)*(T1(I)-T1(IWALL))                                        204    .204
562 BKCN=BKCN+UR(I)*(CN1(I)-CN1(IWALL))                                      205    .205
563 BKCT=BKCT+UR(I)*(CT1(I)-CT1(IWALL))                                      206    .206
564 BKCP=BKCP+UR(I)*(CP1(I)-CP1(IWALL))                                      207    .207  .208
565 BLKT=(UR(1)*(T1(1)-T1(IWALL))+BLKT)/ARVEL+T1(IWALL)                      208    .209
566 BKCN=(UR(1)*(CN1(1)-CN1(IWALL))+BKCN)/ARVEL+CN1(IWALL)                   209    .210
567 BKCT=(UR(1)*(CT1(1)-CT1(IWALL))+BKCT)/ARVEL+CT1(IWALL)                   210    .211
568 BKCP=(UR(1)*(CP1(1)-CP1(IWALL))+BKCP)/ARVEL+CP1(IWALL)                   211    .212
    GO TO (569,1001)ISPT                                                     212    .213

COMPILER EXPECTS A COMMA BETWEEN BRANCH SYMBOL AND BRANCH LIST.

SOURCE ERROR 232. LEVEL 1.    WARNING ONLY.

569 WRITE (6,16) TT,X,TE                                                     213    .214  .215  .216
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        MAIN                                              07/27/65                          PAGE  5
   EXTERNAL FORMULA NUMBER   -   SOURCE STATEMENT   -   INTERNAL FORMULA NUMBER(S)

   570 WRITE (6,17) BLKT                                            214    .217  .218  .219
   571 WRITE (6,18) (T1(I),I=1,IWALL)                               215    .220  .221  .222  .223  .224
   572 WRITE (6,19) SKCT                                            216    .225  .226  .227
   573 WRITE (6,18) (CT1(I),I=1,IWALL)                              217    .228  .229  .230  .231  .232
   574 WRITE (6,20) SKCN                                            218    .233  .234  .235
   575 WRITE (6,18)(CN1(I),I=1,IWALL)                               219    .236  .237  .238  .239  .240
   576 WRITE (6,21) SKCP                                            220    .241  .242  .243
   577 WRITE (6,18) (CP1(I),I=1,IWALL)                              221    .244  .245  .246  .247  .248
   600 IF(X-XPX)602,602,601                                         222    .249
   601 GO TO 30                                                     223    .250
   602 ICNT=1                                                       224    .251
   603 GO TO 605                                                    225    .252
   604 ICNT=ICNT+1                                                  226    .253
   605 X=X+DELX                                                     227    .254
   606 TT=TT+DELT                                                   228    .255
   607 DO 611 I=1,IWALL                                             229    .256
   608 T1(I)=T2(I)                                                  230    .257
   609 CN1(I)=CN2(I)                                                231    .258
   610 CT1(I)=CT2(I)                                                232    .259
   611 CP1(I)=CP2(I)                                                233    .260  .261
   612 GO TO 36                                                     234    .262
  1001  IF(IFLAG)1003,1003,1002                                     235    .263
  1002  WRITE (6,1005)                                              236    .264  .265
        IFLAG=-1                                                    237    .266
  1003  RATIO=SKCP/(SKCP+SKCT)                                      238    .267
        TE=(TE-32.)/1.8                                             239    .268
        BLKTM=(BLKT-32.)/1.8                                        240    .269
        TONEM=(T1(1)-32.)/1.8                                       241    .270
        WRITE (6,1004)TT,X,TE,BLKTM,TONEM,RATIO                     242    .271  .272  .273
        GO TO 600                                                   243    .274
  1004  FORMAT(6E18.7)                                              244
  1005  FORMAT(81X3HCENTER/42X11HENVIRONMENT25X4HLINE/10X4HTIME12X8HDISTAN   245
       1CE8X11HTEMPERATURE10X5HTBULK10X11HTEMPERATURE8X10HCONVERSION)        246
        END                                                         247    .275
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Sample Problem

2D Model of Flow Reactor

Summary of Output Data Not Included with Input Data

Time	period in reactor, hrs.
Distance	position in reactor, ft.
Environment temperature	bath temperature, °C
T_{bulk}	averaged reactant temperature, °C

Centerline temperature, °C

Conversion = moles TVOPA/ moles TVOP input

CTO	moles TVOP/ liter solution (input)
CNO	moles N_2F_4/ liter solution (input)
CPO	moles TVOPA/ liter solution (input)
VEL	reactant velocity, ft/ hr

TWO-DIMENSIONAL MODEL OF LIQUID PHASE FLOW REACTOR, PROGRAM 2

PROBLEM NUMBER 0.1000000E 01

C= 0.2429242E-00	FK= 0.3300000E-01	DEN= 0.9131815E 02	DFI= 0.9000000E-04	DFN= 0.1800000E-03
A= 0.3210000E 13	B= 0.1992000E 05	TAR= 0.4600000E 03	ZZ= 0.1000000E 01	SS= 0.1000000E 01
DELH= 0.4183177E 05	CTC= 0.4685359E-03	CAO= 0.1547060E-02	CPC= 0.	TIO= 0.
DELX= 0.1250000E-01	DELR= 0.7500000E-03	RR= 0.7500000E-02	XMX= 0.1550000E 03	MO= 0.2000000E 03
VEL= 0.3535105E 03	Y= 0.1410000E 03	CON= 0.	CAPR= 0.2040000E-00	LCR= 0.3300000E 01

J= 6 INPT 2 SK= 10 IDTA= 90

XX VALUES	TS VALUES
0.	0.8500000E 02
0.6220000E 02	0.8500000E 02
0.6230000E 02	0.
0.6420000E 02	0.
0.6430000E 02	0.1150000E 03
0.1550000E 03	0.1150000E 03

TIME	DISTANCE	ENVIRONMENT TEMPERATURE	TBULK	CENTER LINE TEMPERATURE	CONVERSION
0.	0.	0.8500000E 02	0.4252667E-00	0.	0.
0.2828770E-02	0.9999993E 00	0.8500000E 02	0.2894345E 02	0.1780945E 01	0.5565641E-03
0.5657527E-02	0.1999999E 01	0.8500000E 02	0.4292871E 02	0.1407043E 02	0.2125493E-02
0.8486303E-02	0.2999998E 01	0.8500000E 02	0.5295094E 02	0.2879558E 02	0.4607519E-02
0.1131504E-01	0.3999997E 01	0.8500000E 02	0.6058370E 02	0.4174382E 02	0.8055105E-02
0.1414383E-01	0.4999996E 01	0.8500000E 02	0.6649982E 02	0.5197901E 02	0.1257522E-01
0.1697259E-01	0.5999995E 01	0.8500000E 02	0.7111718E 02	0.5984374E 02	0.1826785E-01
0.1980135E-01	0.6999994E 01	0.8500000E 02	0.7477933E 02	0.6613496E 02	0.2519173E-01
0.2263011E-01	0.7999993E 01	0.8500000E 02	0.7771015E 02	0.7115808E 02	0.3335146E-01
0.2545887E-01	0.8999987E 01	0.8500000E 02	0.8007984E 02	0.7521923E 02	0.4270018E-01
0.2828764E-01	0.9999982E 01	0.8500000E 02	0.8201559E 02	0.7854322E 02	0.5314961E-01
0.3111640E-01	0.1099998E 02	0.8500000E 02	0.8361045E 02	0.8129313E 02	0.6458221E-01
0.3394516E-01	0.1199997E 02	0.8500000E 02	0.8493276E 02	0.8358689E 02	0.7686221E-01
0.3677392E-01	0.1299996E 02	0.8500000E 02	0.8603296E 02	0.8550982E 02	0.8994445E-01
0.3960268E-01	0.1399996E 02	0.8500000E 02	0.8694853E 02	0.8712419E 02	0.1033512E-00
0.4243145E-01	0.1499995E 02	0.8500000E 02	0.8770769E 02	0.8847598E 02	0.1173268E-00
0.4526021E-0.	0.1599995E 02	0.8500000E 02	0.8833214E 02	0.8960063E 02	0.1315420E-00
0.4808897E-01	0.1599993E 02	0.8500000E 02	0.8883901E 02	0.9052358E 02	0.1459966E-00
0.5091773E-01	0.1799992E 02	0.8500000E 02	0.8924237E 02	0.9126896E 02	0.1602717E-00
0.5374649E-01	0.1899990E 02	0.8500000E 02	0.8955418E 02	0.9185535E 02	0.1745618E-00
0.5657526E-01	0.1999989E 02	0.8500000E 02	0.8976507E 02	0.9230003E 02	0.1886759E-00
0.5940402E-01	0.2099987E 02	0.8500000E 02	0.8994476E 02	0.9261912E 02	0.2025381E-00
0.6223278E-01	0.2199986E 02	0.8500000E 02	0.9004235E 02	0.9282798E 02	0.2160873E-00
0.6506154E-01	0.2299984E 02	0.8500000E 02	0.9008544E 02	0.9294136E 02	0.2292771E-00
0.6789030E-01	0.2399983E 02	0.8500000E 02	0.9008513E 02	0.9297333E 02	0.2420743E-00
0.7071906E-01	0.2499981E 02	0.8500000E 02	0.9004604E 02	0.9293723E 02	0.2544578E-00
0.7354783E-01	0.2599979E 02	0.8500000E 02	0.8997620E 02	0.9284544E 02	0.2664156E-00
0.7637659E-01	0.2699978E 02	0.8500000E 02	0.8988203E 02	0.9270930E 02	0.2779484E-00
0.7920535E-01	0.2799976E 02	0.8500000E 02	0.8976925E 02	0.9253895E 02	0.2890577E-00
0.8203411E-01	0.2899975E 02	0.8500000E 02	0.8964259E 02	0.9234331E 02	0.2997541E-00
0.8486287E-01	0.2999973E 02	0.8500000E 02	0.8950726E 02	0.9213007E 02	0.3100512E-00
0.8769164E-01	0.3099972E 02	0.8500000E 02	0.8936602E 02	0.9190568E 02	0.3199651E-00
0.9052040E-01	0.3199970E 02	0.8500000E 02	0.8922215E 02	0.9167551E 02	0.3295134E-00
0.9334916E-01	0.3299969E 02	0.8500000E 02	0.8907806E 02	0.9144354E 02	0.3387145E-00
0.9617792E-01	0.3399967E 02	0.8500000E 02	0.8893567E 02	0.9121409E 02	0.3475878E-00
0.9900668E-01	0.3499966E 02	0.8500000E 02	0.8879641E 02	0.9098883E 02	0.3561510E-00
0.1018354E-00	0.3599964E 02	0.8500000E 02	0.8866135E 02	0.9077001E 02	0.3644222E-00
0.1046642E-00	0.3699963E 02	0.8500000E 02	0.8853122E 02	0.9055898E 02	0.3724184E-00
0.1074930E-00	0.3799961E 02	0.8500000E 02	0.8840651E 02	0.9035661E 02	0.3801563E-00
0.1103217E-00	0.3899960E 02	0.8500000E 02	0.8828747E 02	0.9016343E 02	0.3876506E-00
0.1131505E-00	0.3999958E 02	0.8500000E 02	0.8817422E 02	0.8997967E 02	0.3949156E-00
0.1159793E-00	0.4099957E 02	0.8500000E 02	0.8806674E 02	0.8980534E 02	0.4019646E-00
0.1188080E-00	0.4199955E 02	0.8500000E 02	0.8796489E 02	0.8964027E 02	0.4085093E-00

0.1216348E-00	0.4299954E 02	0.8500000E 02	0.8786851E 02	0.8948419E 02	0.4154624E-00
0.1244655E-00	0.4399952E 02	0.8500000E 02	0.8777735E 02	0.8933672E 02	0.4219330E-00
0.1272942E-00	0.4499950E 02	0.8500000E 02	0.8769119E 02	0.8919745E 02	0.4282313E-00
0.1301229E-00	0.4599949E 02	0.8500000E 02	0.8760971E 02	0.8906592E 02	0.4343660E-00
0.1329516E-00	0.4699947E 02	0.8500000E 02	0.8753265E 02	0.8894168E 02	0.4403455E-00
0.1357803E-00	0.4799946E 02	0.8500000E 02	0.8745975E 02	0.8882427E 02	0.4461772E-00
0.1386090E-00	0.4899944E 02	0.8500000E 02	0.8739067E 02	0.8871322E 02	0.4518684E-00
0.1414377E-00	0.4999943E 02	0.8500000E 02	0.8732521E 02	0.8860811E 02	0.4574254E-00
0.1442564E-00	0.5099941E 02	0.8500000E 02	0.8726311E 02	0.8850852E 02	0.4628543E-00
0.1470951E-00	0.5199940E 02	0.8500000E 02	0.8720423E 02	0.8841406E 02	0.4681609E-00
0.1499237E-00	0.5299938E 02	0.8500000E 02	0.8714805E 02	0.8832435E 02	0.4733509E-00
0.1527524E-00	0.5399937E 02	0.8500000E 02	0.8709465E 02	0.8823903E 02	0.4784267E-00
0.1555811E-00	0.5499935E 02	0.8500000E 02	0.8704378E 02	0.8815792E 02	0.4833957E-00
0.1584098E-00	0.5599934E 02	0.8500000E 02	0.8699523E 02	0.8808057E 02	0.4882609E-00
0.1612385E-00	0.5699932E 02	0.8500000E 02	0.8694855E 02	0.8800478E 02	0.4930266E-00
0.1640672E-00	0.5799931E 02	0.8500000E 02	0.8690449E 02	0.8793628E 02	0.4976964E-00
0.1668959E-00	0.5899929E 02	0.8500000E 02	0.8686201E 02	0.8786985E 02	0.5022737E 00
0.1697246E-00	0.5999928E 02	0.8500000E 02	0.8682130E 02	0.8780430E 02	0.5067620E 00
0.1725532E-00	0.6099926E 02	0.8500000E 02	0.8678224E 02	0.8774243E 02	0.5111643E 00
0.1753119E-00	0.6199924E 02	0.8500000E 02	0.8674472E 02	0.8768307E 02	0.5154535E 00
0.1782106E-00	0.6299923E 02	0.	0.6261625E 02	0.6717718E 02	0.5179543E 00
0.1810393E-00	0.6399921E 02	0.	0.4668294E 02	0.7719830E 02	0.5185269E 00
0.1838680E-00	0.6499920E 02	0.1150000E 03	0.6309511E 02	0.6250229E 02	0.5199309E 00
0.1866967E-00	0.6599918E 02	0.1150000E 03	0.8125711E 02	0.6161253E 02	0.5256974E 00
0.1895254E-00	0.6699917E 02	0.1150000E 03	0.8995874E 02	0.7113859E 02	0.5347922E 00
0.1923541E-00	0.6799915E 02	0.1150000E 03	0.9655735E 02	0.8129722E 02	0.5465333E 00
0.1951827E-00	0.6899914E 02	0.1150000E 03	0.1018127E 03	0.8999714E 02	0.5607464E 00
0.1980114E-00	0.6999912E 02	0.1150000E 03	0.1061036E 03	0.9727914E 02	0.5773414E 00
0.2008401E-00	0.7099911E 02	0.1150000E 03	0.1096733E 03	0.1034449E 03	0.5961466E 00
0.2036688E-00	0.7199909E 02	0.1150000E 03	0.1126758E 03	0.1087456E 03	0.6153352E 00
0.2064975E-00	0.7299908E 02	0.1150000E 03	0.1152064E 03	0.1133715E 03	0.6389770E 00
0.2093262E-00	0.7399906E 02	0.1150000E 03	0.1173162E 03	0.1172603E 03	0.6629397E 00
0.2121549E-00	0.7499905E 02	0.1150000E 03	0.1190244E 03	0.1203273E 03	0.6852042E 00
0.2149836E-00	0.7599903E 02	0.1150000E 03	0.1203441E 03	0.1230486E 03	0.7079216E 00
0.2178122E-00	0.7699902E 02	0.1150000E 03	0.1212161E 03	0.1249572E 03	0.7295022E 00
0.2206409E-00	0.7799900E 02	0.1150000E 03	0.1218313E 03	0.1261304E 03	0.7494785E 00
0.2234696E-00	0.7899899E 02	0.1150000E 03	0.1221059E 03	0.1269635E 03	0.7675593E 00
0.2262983E-00	0.7999897E 02	0.1150000E 03	0.1220993E 03	0.1267685E 03	0.7835100E 00
0.2291270E-00	0.8099895E 02	0.1150000E 03	0.1218959E 03	0.1264736E 03	0.7976898E 00
0.2319557E-00	0.8199894E 02	0.1150000E 03	0.1215573E 03	0.1259289E 03	0.8103387E 00
0.2347844E-00	0.8299892E 02	0.1150000E 03	0.1211371E 03	0.1252337E 03	0.8215777E 00
0.2376131E-00	0.8399891E 02	0.1150000E 03	0.1206771E 03	0.1244644E 03	0.8310714E 00
0.2404417E-00	0.8499889E 02	0.1150000E 03	0.1202083E 03	0.1236762E 03	0.8395679E 00
0.2432704E-00	0.8599888E 02	0.1150000E 03	0.1197515E 03	0.1229060E 03	0.8473403E 00
0.2460991E-00	0.8699886E 02	0.1150000E 03	0.1193198E 03	0.1221771E 03	0.8542392E 00
0.2489278E-00	0.8799885E 02	0.1150000E 03	0.1189205E 03	0.1215076E 03	0.8604737E 00
0.2517564E-00	0.8899883E 02	0.1150000E 03	0.1185569E 03	0.1208881E 03	0.8661553E 00
0.2545849E-00	0.8999882E 02	0.1150000E 03	0.1182293E 03	0.1203347E 03	0.8713631E 00
0.2574135E-00	0.9099880E 02	0.1150000E 03	0.1179365E 03	0.1198404E 03	0.8761624E 00
0.2602420E-00	0.9199879E 02	0.1150000E 03	0.1176762E 03	0.1194013E 03	0.8806084E 00
0.2630706E-00	0.9299877E 02	0.1150000E 03	0.1174456E 03	0.1190127E 03	0.8847482E 00
0.2658991E-00	0.9399876E 02	0.1150000E 03	0.1172417E 03	0.1186694E 03	0.8886132E 00
0.2687276E-00	0.9499874E 02	0.1150000E 03	0.1170615E 03	0.1183664E 03	0.8922405E 00
0.2715562E-00	0.9599873E 02	0.1150000E 03	0.1169021E 03	0.1180992E 03	0.8956540E 00
0.2743847E-00	0.9699871E 02	0.1150000E 03	0.1167610E 03	0.1178626E 03	0.8988759E 00
0.2772132E-00	0.9799870E 02	0.1150000E 03	0.1166358E 03	0.1176533E 03	0.9019245E 00
0.2800418E-00	0.9899868E 02	0.1150000E 03	0.1165245E 03	0.1174675E 03	0.9048159E 00

0.28287063E-00	0.99998665E 02	0.11500000E 03	0.11642538E 03	0.11730228E 03	0.90756598E 00
0.28569895E-00	0.10099935E 03	0.11500000E 03	0.11633645E 03	0.11715465E 03	0.91018358E 00
0.28852745E-00	0.10199986E 03	0.11500000E 03	0.11625448E 03	0.11702238E 03	0.91265088E 00
0.29135595E-00	0.10299986E 03	0.11500000E 03	0.11618478E 03	0.11690328E 03	0.91506668E 00
0.29418445E-00	0.10399986E 03	0.11500000E 03	0.11611978E 03	0.11679578E 03	0.91734918E 00
0.29701305E-00	0.10499986E 03	0.11500000E 03	0.11606068E 03	0.11669935E 03	0.91953578E 00
0.29984165E-00	0.10599986E 03	0.11500000E 03	0.11600675E 03	0.11660978E 03	0.92163278E 00
0.30267016E-00	0.10699986E 03	0.11500000E 03	0.11595748E 03	0.11652978E 03	0.92364608E 00
0.30549865E-00	0.10799985E 03	0.11500000E 03	0.11591215E 03	0.11645465E 03	0.92558108E 00
0.30832727E-00	0.10899985E 03	0.11500000E 03	0.11587045E 03	0.11638643E 03	0.92744228E 00
0.31115578E-00	0.10999985E 03	0.11500000E 03	0.11583198E 03	0.11632338E 03	0.92923418E 00
0.31398428E-00	0.11099985E 03	0.11500000E 03	0.11579608E 03	0.11626508E 03	0.93095078E 00
0.31681285E-00	0.11199985E 03	0.11500000E 03	0.11576285E 03	0.11621098E 03	0.93262558E 00
0.31964135E-00	0.11299985E 03	0.11500000E 03	0.11573178E 03	0.11616058E 03	0.93423208E 00
0.32246995E-00	0.11399985E 03	0.11500000E 03	0.11570277E 03	0.11611348E 03	0.93578318E 00
0.32529845E-00	0.11499984E 03	0.11500000E 03	0.11567555E 03	0.11606938E 03	0.93728188E 00
0.32812695E-00	0.11599984E 03	0.11500000E 03	0.11565005E 03	0.11602808E 03	0.93873058E 00
0.33095555E-00	0.11699984E 03	0.11500000E 03	0.11562605E 03	0.11598928E 03	0.94013208E 00
0.33378405E-00	0.11799984E 03	0.11500000E 03	0.11560338E 03	0.11595268E 03	0.94148838E 00
0.33661265E-00	0.11899984E 03	0.11500000E 03	0.11558198E 03	0.11591818E 03	0.94280158E 00
0.33944115E-00	0.11999984E 03	0.11500000E 03	0.11556175E 03	0.11588548E 03	0.94407398E 00
0.34226965E-00	0.12099983E 03	0.11500000E 03	0.11554255E 03	0.11585465E 03	0.94530708E 00
0.34509825E-00	0.12199983E 03	0.11500000E 03	0.11552438E 03	0.11582538E 03	0.94650288E 00
0.34792675E-00	0.12299983E 03	0.11500000E 03	0.11550705E 03	0.11579758E 03	0.94766258E 00
0.35075525E-00	0.12399983E 03	0.11500000E 03	0.11549055E 03	0.11577118E 03	0.94878818E 00
0.35358385E-00	0.12499983E 03	0.11500000E 03	0.11547458E 03	0.11574608E 03	0.94988028E 00
0.35641235E-00	0.12599983E 03	0.11500000E 03	0.11545998E 03	0.11572208E 03	0.95094218E 00
0.35924095E-00	0.12699983E 03	0.11500000E 03	0.11544565E 03	0.11569928E 03	0.95197328E 00
0.36206945E-00	0.12799982E 03	0.11500000E 03	0.11543205E 03	0.11567748E 03	0.95297538E 00
0.36489795E-00	0.12899981E 03	0.11500000E 03	0.11541905E 03	0.11565668E 03	0.95394958E 00
0.36772655E-00	0.12999981E 03	0.11500000E 03	0.11540655E 03	0.11563678E 03	0.95489698E 00
0.37055505E-00	0.13099980E 03	0.11500000E 03	0.11539545E 03	0.11561768E 03	0.95581878E 00
0.37338365E-00	0.13199979E 03	0.11500000E 03	0.11538318E 03	0.11559948E 03	0.95671568E 00
0.37621215E-00	0.13299978E 03	0.11500000E 03	0.11537228E 03	0.11558198E 03	0.95758878E 00
0.37904065E-00	0.13399977E 03	0.11500000E 03	0.11536165E 03	0.11556518E 03	0.95843888E 00
0.38186925E-00	0.13499976E 03	0.11500000E 03	0.11535155E 03	0.11554918E 03	0.95926558E 00
0.38469775E-00	0.13599975E 03	0.11500000E 03	0.11534188E 03	0.11553368E 03	0.96007348E 00
0.38752625E-00	0.13699974E 03	0.11500000E 03	0.11533245E 03	0.11551878E 03	0.96085948E 00
0.39035485E-00	0.13799973E 03	0.11500000E 03	0.11532345E 03	0.11550458E 03	0.96162558E 00
0.39318335E-00	0.13899972E 03	0.11500000E 03	0.11531485E 03	0.11549078E 03	0.96237248E 00
0.39601195E-00	0.13999971E 03	0.11500000E 03	0.11530645E 03	0.11547758E 03	0.96310088E 00
0.39884045E-00	0.14099972E 03	0.11500000E 03	0.11529848E 03	0.11546488E 03	0.96381128E 00
0.40166895E-00	0.14199969E 03	0.11500000E 03	0.11529065E 03	0.11545258E 03	0.96450438E 00
0.40449755E-00	0.14299969E 03	0.11500000E 03	0.11528325E 03	0.11544078E 03	0.96518068E 00
0.40732605E-00	0.14399968E 03	0.11500000E 03	0.11527595E 03	0.11542938E 03	0.96584078E 00
0.41015465E-00	0.14499967E 03	0.11500000E 03	0.11526908E 03	0.11541828E 03	0.96648508E 00
0.41298315E-00	0.14599966E 03	0.11500000E 03	0.11526228E 03	0.11540768E 03	0.96711428E 00
0.41581175E-00	0.14699965E 03	0.11500000E 03	0.11525578E 03	0.11539748E 03	0.96772858E 00
0.41864025E-00	0.14799964E 03	0.11500000E 03	0.11524945E 03	0.11538748E 03	0.96832858E 00
0.42146875E-00	0.14899963E 03	0.11500000E 03	0.11524345E 03	0.11537798E 03	0.96891518E 00
0.42429735E-00	0.14999962E 03	0.11500000E 03	0.11523758E 03	0.11536858E 03	0.96948808E 00
0.42712585E-00	0.15099961E 03	0.11500000E 03	0.11523188E 03	0.11535958E 03	0.97004788E 00
0.42995435E-00	0.15199960E 03	0.11500000E 03	0.11522638E 03	0.11535098E 03	0.97059518E 00
0.43278295E-00	0.15299959E 03	0.11500000E 03	0.11522098E 03	0.11534258E 03	0.97113018E 00
0.43561145E-00	0.15399959E 03	0.11500000E 03	0.11521598E 03	0.11533448E 03	0.97165318E 00
0.43843995E-00	0.15499958E 03	0.11500000E 03	0.11521088E 03	0.11532658E 03	0.97216478E 00
0.44126855E-00	0.15599957E 03	-0.17777777E 02	0.70683258E 02	0.11279988E 03	0.97235028E 00

Bulk Flow Model Computer Program

Input Data for Bulk Flow Model Computer Program

Fortran Symbol	Meaning	Units for 0.16" I.D. Tubing
XMX	Maximum length in reactor	______ ft.
DELT	Time increment for calculations	______ hrs.
HI	Inside tube heat transfer coefficient	8.85 BTU/hr-ft^2-°F
HO	Outside tube heat transfer coefficient	220 BTU/hr-ft^2-°F
CW	Thermal conductance through tube wall	3000 BTU/hr-ft^2-°F
A	Pre-exponential factor	3.21×10^{17} 1/hr
B	(E/R) constant in rate exponential	1.11×10^4 °C
TAR	Constant to convert to absolute temperature	273 °C to °K
AA	Exponent in rate expression	1.0
BB	Exponent in rate expression	1.0
R	Radius of tube	7.5×10^{-3} ft.
FLCR	Mole ratio N_2F_4/TVOP at 0% conversion	______ gm moles N_2F_4/gm moles TVOP
CAPR	Gms. N_2F_4/cc solvent at 0% conversion	______ gms N_2F_4/cc solvent
Y	TVOP feed rate	______ gms/hr
TIO	Initial temperature of fluid entering reactor	10°C
PROB	Problem identification number	______
FC	Initial fraction reacted (0 if problem starts with 1st stage)	______
j[a]	Number of points to describe environment temperature	______
IBTA[b]	Printout frequency	______
XX(1)	Distance to 1st environment temperature point	0 ft.
TS (1)	Temperature of 1st environment temperature point	______ °C
XX(2)	Distance to 2nd environment temperature point	______ ft.
TS(2)	Temperature at 2nd environment temperature point	______ °C
XX(j)	Distance to jth environment temperature point	______ ft.
TS(j)	Temperature at jth environment temperature point	______ °C

(a) [XX(1), TS(1)], [XX(2), TS(2)], etc. are considered pairs and j instructs the computer about the number of pairs to be read.

(b) If for example IBTA is 5, the calculator is instructed to print every fifth calculation it makes.

FORTRAN Listing

Bulk Model of Flow Reactor

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00000  *     PROGRAM NO. 65
00000  C     BULK ANALYSIS  II - LIQUID PHASE FLOW REACTOR
00000  C     DON WILLOUGHBY,ROHM AND HAAS COMPANY                3/13/65
00001        DIMENSION TS(500),XX(500)
00001  10    FORMAT(5E14.7)
00007  11    FORMAT(2I5)
00014  12    FORMAT(16H1PROBLEM NUMBER ,E14.7/)
00034  13    FORMAT(25H EQUATIONS UNSTABLE, STOP)
00035  14    FORMAT(8H    XMK=E14.7,8H   DELT=E14.7,8H     WI=E14.7,     8H
00035       1 WO=E14.7,8H     WW=E14.7)
00132  15    FORMAT(8H      A=E14.7,8H      B=E14.7,8H    TAR=E14.7,8H     AA=
00132       1E14.7,8H     BB=E14.7)
00205  16    FORMAT(8H      R=E14.7,8H   FLCR=E14.7,8H   CAPR=E14.7,8H      Y=
00205       1E14.7,8H    T10=E14.7)
00260  17    FORMAT(8H      J=I5,12H      IBTA=I5)
00302  18    FORMAT(20H      XX              TS      )
00325  19    FORMAT(2E14.7)
00333  20    FORMAT(8H    CTO=E14.7,8H    CNO=E14.7,8H    DEN=E14.7,8H   DELN=
00333       1E14.7,8H      C=E14.7)
00406  21    FORMAT(9E13.5)
00414  22    FORMAT(3X10HTIME HOURS5X10HX-FEET3X12HBULK TEMP.-C13X F NOT CONVTDG
00414       1X3HCT115X3HCN118X3HCP17X10HWALL TEMP.7X2HTS)
00502  30    READ 10, XMK,DELT,WI,WO,WW,A,B,TAR,AA,BB,R,FLCR,CAPR,Y,T10,
00502       1PROB,FC
00547  31    READ 11,J,IBTA
00556  32    READ10,(XX(I),TS(I),I=1,J)
00602  33    PRINT 12,PROB
00607  34    PRINT 14,XMK,DELT,WI,WO,WW
00624  35    PRINT 15, A,B,TAR,AA,BB
00641  36    PRINT 16,R,FLCR,CAPR,Y,T10
00656  37    PRINT 17,J,IBTA
00665  38    PRINT 18
00670  39    PRINT 19,(XX(I),TS(I),I=1,J)
00714  40    CNO=CAPR/(104.0+CAPR*(83.0+176.0/FLCR))
00736  41    CTO=CNO/FLCR
00744  42    CPO=0.0
00750  43    V1=83.1*CNO
00756  44    V2=176.0*CTO
00764  45    VS=1.0-V1-V2
00774  46    DEN=(104.0*CNO+178.0*CTO+1.95*VS)*62.4
01024  47    DELN=3020000.0/DEN
01032  48    X3=0.00465*VS
01040  49    X4=0.0025*VS
01046  50    AX=X3+X4+CNO+CTO
01060  51    Y1=CNO/AX
01066  52    Y2=CTO/AX
01074  53    Y3=X3/AX
01102  54    Y4=X4/AX
01110  55    C=(Y1*0.29+Y2*0.46+Y3*0.213+Y4*0.234)
01146  56    PRINT 20,CTO,CNO,DEN,DELN,C
01163        C=C*1.0
01171  57    T1=T10
01175  58    CT1=CTO
01201  59    CN1=CNO
01205  60    CP1=CPO
```

```
01211  552   CP1=FC*CTC
01217  553   CT1=CT1-CP1
01225  554   CM1=CM1-3.0*CP1
01234  61    AREA=3.1416*R*R
01244  62    VEL=Y/(270.0*CT0*AREA*28317.0)
01256  65    TT=0.0
01272  66    X=0.0
01276  67    ICNT=IBTA
01302  68    UT=1.0/MI+1.0/ME+1.0/MW
01330  69    U=1.0/UT+9.0/5.0
01342        MI=MI+1.0
01350  70    CC=DELT/DEN*U/C*2.0/R
01366  71    C1=1.0-CC
01374  72    IF(C1) 73,73,75
01402  73    PRINT 13
01405  74    GO TO 38
01407  75    C2=CC
01413  76    C0=-DELM/C
01422  77    DELX=VEL*DELT
01430  80    J=1
01434  81    XM=(TS(2)-TS(1))/(XX(2)-XX(1))
01442  89    PRINT 22
01465  90    IF(XX(J+1)-X) 91,94,94
01505  91    J=J+1
01513  92    XM=(TS(J+1)-TS(J))/(XX(J+1)-XX(J))
01555  93    GO TO 90
01557  94    TE=TS(J+1)-XM*(XX(J+1)-X)
01612  100   DELCM=-A*EXP (-B/(T1+TAR))*CM1**AA*CT1**BB*DELT
01664  101   CM2=CM1+DELCM
01672  102   IF(CM2)103,105,105
01700  103   CM2=0.0
01704  104   DELCM=-CM1
01711  105   CT2=CT1+DELCM/3.0
01721  106   IF(CT2)107,111,111
01727  107   CT2=0.0
01733  108   DELCT=-CT1
01740  109   DELCM=3.0*DELCT
01746  110   CM2=CM1+DELCM
01754  111   CONTINUE
01754  112   CP2=CP1-DELCM/3.0
01765  150   T2=C1*T1+C2*TE+C0*DELCM
02013  156   TB=T1+C/MI*(TE-T1)
02033  157   F=CT1/CT0
02041  160   IF(ICNT-IBTA)166,161,161
02051  161   PRINT 21,TT,X,T1,F,CT1,CM1,CP1,TB,TE
02070  162   IF(X-XMX)164,164,163
02106  163   GO TO 38
02115  164   ICNT=1
02114  165   GO TO 167
02116  166   ICNT=ICNT+1
02124  167   X=X+DELX
02132  168   TT=TT+DELT
02140  169   T1=T2
02144  170   CT1=CT2
02150  171   CM1=CM2
02154  172   CP1=CP2
```

Sample Problem

Bulk Model of Flow Reactor

Summary of Output Data Not Included With Input Data

Time	period in reactor, hrs.
[illegible]-feet	position in reactor, ft.
F NOT CONVTD	moles TVOP/ moles TVOP input
BULK TEMP-°C	Reactant temperature, °C
CT1	moles TVOP/ liter of solution
CN1	moles N_2F_4/ liter of solution
CP1	moles TVOPA/ liter of solution
Wall temperature	temperature of tube wall, °C
TS	bath temperature, °C

```
PROBLEM NUMBER  0.1000000E 01

   XMI= 0.1550000E 03   DELT= 0.1000000E-02     KI= 0.8050000E 01     HC= 0.2000000E 03     WW= 0.3000000E 04
     A= 0.3210000E 10      B= 0.1110000E 05    TAR= 0.2730000E 03     AA= 0.1000000E 01     BB= 0.1000000E 01
     R= 0.7500000E-02   FLCR= 0.3300000E 01   CAPR= 0.2040000E 00      Y= 0.1410000E 03    T1D= 0.0000000E 00
     J=    6          IOTA=    5
     XX               TS
0.0000000E 00 0.8500000E 02
0.6220000E 02 0.8500000E 02
0.6230000E 02 0.0000000E 00
0.6420000E 02 0.0000000E 00
0.6430000E 02 0.1150000E 03
0.1550000E 03 0.1150000E 03
   CTO= 0.4609875E-03    CMO= 0.1547659E-02    DEN= 0.9131606E 02    DELH= 0.4183273E 05    C= 0.2429335E 00
```

TIME HOURS	X-FEET	BULK TEMP.-C	F NOT CONVTD	CT1	CR1	CP1	WALL TEMP.	TS
0.00000E 00	0.00000E 00	0.00000E 00	0.10000E 01	0.46099E-03	0.15477E-02	0.00000E 00	0.81169E 02	0.85000E 02
0.50000E-02	0.17671E 01	0.35254E 02	0.99997E 00	0.46097E-03	0.15476E-02	0.15816E-07	0.82750E 02	0.85000E 02
0.10000E-01	0.35342E 01	0.55963E 02	0.99931E 00	0.46066E-03	0.15467E-02	0.32311E-06	0.83691E 02	0.85000E 02
0.15000E-01	0.53013E 01	0.68394E 02	0.99594E 00	0.45786E-03	0.15419E-02	0.19634E-05	0.84252E 02	0.85000E 02
0.20000E-01	0.70684E 01	0.76269E 02	0.98722E 00	0.46306E-03	0.15287E-02	0.59921E-05	0.84606E 02	0.85000E 02
0.25000E-01	0.88354E 01	0.81642E 02	0.97159E 00	0.45566E-03	0.15077E-02	0.13325E-04	0.84849E 02	0.85000E 02
0.30000E-01	0.10603E 02	0.85577E 02	0.94879E 00	0.44495E-03	0.14756E-02	0.24034E-04	0.85026E 02	0.85000E 02
0.35000E-01	0.12370E 02	0.88600E 02	0.91932E 00	0.43115E-03	0.14341E-02	0.37837E-04	0.85162E 02	0.85000E 02
0.40000E-01	0.14137E 02	0.90949E 02	0.88455E 00	0.41484E-03	0.13852E-02	0.54144E-04	0.85268E 02	0.85000E 02
0.45000E-01	0.15904E 02	0.92713E 02	0.84616E 00	0.39604E-03	0.13312E-02	0.72148E-04	0.85340E 02	0.85000E 02
0.50000E-01	0.17671E 02	0.93908E 02	0.80620E 00	0.37828E-03	0.12750E-02	0.90608E-04	0.85401E 02	0.85000E 02
0.55000E-01	0.19438E 02	0.94540E 02	0.76677E 00	0.35968E-03	0.12195E-02	0.10930E-03	0.85430E 02	0.85000E 02
0.60000E-01	0.21205E 02	0.94652E 02	0.72962E 00	0.34218E-03	0.11672E-02	0.12600E-03	0.85435E 02	0.85000E 02
0.65000E-01	0.22972E 02	0.94335E 02	0.69592E 00	0.32630E-03	0.11190E-02	0.14241E-03	0.85421E 02	0.85000E 02
0.70000E-01	0.24739E 02	0.93721E 02	0.66611E 00	0.31248E-03	0.10779E-02	0.15659E-03	0.85393E 02	0.85000E 02
0.75000E-01	0.26506E 02	0.92949E 02	0.64000E 00	0.30819E-03	0.10413E-02	0.16800E-03	0.85358E 02	0.85000E 02
0.80000E-01	0.28273E 02	0.92130E 02	0.61740E 00	0.28955E-03	0.10093E-02	0.17944E-03	0.85321E 02	0.85000E 02
0.85000E-01	0.30041E 02	0.91345E 02	0.59752E 00	0.28023E-03	0.98130E-03	0.18876E-03	0.85286E 02	0.85000E 02
0.90000E-01	0.31808E 02	0.90630E 02	0.57998E 00	0.27198E-03	0.95663E-03	0.19701E-03	0.85254E 02	0.85000E 02
0.95000E-01	0.33575E 02	0.90024E 02	0.56416E 00	0.26458E-03	0.93445E-03	0.20440E-03	0.85226E 02	0.85000E 02
0.10000E 00	0.35342E 02	0.89585E 02	0.54987E 00	0.25788E-03	0.91424E-03	0.21110E-03	0.85203E 02	0.85000E 02
0.10500E 00	0.37109E 02	0.89071E 02	0.53677E 00	0.25174E-03	0.89592E-03	0.21725E-03	0.85183E 02	0.85000E 02
0.11000E 00	0.38876E 02	0.88719E 02	0.52465E 00	0.24585E-03	0.87886E-03	0.22293E-03	0.85167E 02	0.85000E 02
0.11500E 00	0.40643E 02	0.88410E 02	0.51335E 00	0.24076E-03	0.86296E-03	0.22823E-03	0.85154E 02	0.85000E 02
0.12000E 00	0.42410E 02	0.88159E 02	0.50274E 00	0.23570E-03	0.84803E-03	0.23321E-03	0.85142E 02	0.85000E 02
0.12500E 00	0.44177E 02	0.87947E 02	0.49272E 00	0.23100E-03	0.83394E-03	0.23791E-03	0.85133E 02	0.85000E 02
0.13000E 00	0.45944E 02	0.87760E 02	0.48323E 00	0.22663E-03	0.82058E-03	0.24236E-03	0.85125E 02	0.85000E 02
0.13500E 00	0.47711E 02	0.87618E 02	0.47419E 00	0.22239E-03	0.80787E-03	0.24660E-03	0.85118E 02	0.85000E 02
0.14000E 00	0.49478E 02	0.87473E 02	0.46557E 00	0.21835E-03	0.79573E-03	0.25064E-03	0.85111E 02	0.85000E 02
0.14500E 00	0.51246E 02	0.87353E 02	0.45732E 00	0.21448E-03	0.78413E-03	0.25451E-03	0.85106E 02	0.85000E 02
0.15000E 00	0.53013E 02	0.87245E 02	0.44941E 00	0.21077E-03	0.77300E-03	0.25822E-03	0.85101E 02	0.85000E 02
0.15500E 00	0.54780E 02	0.87147E 02	0.44181E 00	0.20720E-03	0.76231E-03	0.26178E-03	0.85097E 02	0.85000E 02
0.16000E 00	0.56547E 02	0.87059E 02	0.43450E 00	0.20378E-03	0.75203E-03	0.26521E-03	0.85093E 02	0.85000E 02
0.16500E 00	0.58314E 02	0.86977E 02	0.42746E 00	0.20047E-03	0.74212E-03	0.26851E-03	0.85089E 02	0.85000E 02
0.17000E 00	0.60081E 02	0.86903E 02	0.42067E 00	0.19729E-03	0.73256E-03	0.27170E-03	0.85086E 02	0.85000E 02
0.17500E 00	0.61848E 02	0.86833E 02	0.41411E 00	0.19421E-03	0.72334E-03	0.27477E-03	0.85083E 02	0.85000E 02
0.18000E 00	0.63615E 02	0.63896E 02	0.40943E 00	0.19202E-03	0.71679E-03	0.27697E-03	0.20440E 01	0.00000E 00
0.18500E 00	0.65382E 02	0.68993E 02	0.40095E 00	0.19179E-03	0.71607E-03	0.27720E-03	0.11291E 03	0.11500E 03
0.19000E 00	0.67149E 02	0.84195E 02	0.40502E 00	0.19037E-03	0.72181E-03	0.27842E-03	0.11379E 03	0.11500E 03
0.19500E 00	0.68916E 02	0.10059E 03	0.39477E 00	0.18514E-03	0.69612E-03	0.28305E-03	0.11435E 03	0.11500E 03
0.20000E 00	0.70684E 02	0.10925E 03	0.37009E 00	0.17394E-03	0.66253E-03	0.29584E-03	0.11474E 03	0.11500E 03
0.20500E 00	0.72451E 02	0.11577E 03	0.33379E 00	0.15654E-03	0.61033E-03	0.31244E-03	0.11503E 03	0.11500E 03
0.21000E 00	0.74218E 02	0.12049E 03	0.28814E 00	0.13513E-03	0.54618E-03	0.33309E-03	0.11525E 03	0.11500E 03
0.21500E 00	0.75985E 02	0.12324E 03	0.24221E 00	0.11359E-03	0.48140E-03	0.35539E-03	0.11537E 03	0.11500E 03
0.22000E 00	0.77752E 02	0.12404E 03	0.20312E 00	0.95262E-04	0.42640E-03	0.37373E-03	0.11541E 03	0.11500E 03
0.22500E 00	0.79519E 02	0.12356E 03	0.17320E 00	0.81229E-04	0.38430E-03	0.38778E-03	0.11539E 03	0.11500E 03

0.23000E 00	0.81246E 02	0.12243E 03	0.15133E 00	0.70876E-04	0.35332E-03	0.39911E-03	0.11533E 03	0.11590E 03
0.23500E 00	0.83053E 02	0.12112E 03	0.13466E 00	0.63154E-04	0.33616E-03	0.40583E-03	0.11528E 03	0.11589E 03
0.24000E 00	0.84920E 02	0.11995E 03	0.12197E 00	0.57285E-04	0.31231E-03	0.41172E-03	0.11522E 03	0.11589E 03
0.24500E 00	0.86567E 02	0.11901E 03	0.11163E 00	0.52448E-04	0.29884E-03	0.41654E-03	0.11518E 03	0.11590E 03
0.25000E 00	0.88354E 02	0.11826E 03	0.10345E 00	0.48515E-04	0.28824E-03	0.42047E-03	0.11515E 03	0.11588E 03
0.25500E 00	0.90121E 02	0.11769E 03	0.95321E-01	0.45173E-04	0.27622E-03	0.42381E-03	0.11512E 03	0.11588E 03
0.26000E 00	0.91849E 02	0.11725E 03	0.89134E-01	0.42272E-04	0.26751E-03	0.42672E-03	0.11510E 03	0.11588E 03
0.26500E 00	0.93656E 02	0.11691E 03	0.84672E-01	0.39716E-04	0.25983E-03	0.42928E-03	0.11509E 03	0.11588E 03
0.27000E 00	0.95423E 02	0.11665E 03	0.79786E-01	0.37419E-04	0.25295E-03	0.43157E-03	0.11507E 03	0.11588E 03
0.27500E 00	0.97193E 02	0.11645E 03	0.75372E-01	0.35349E-04	0.24674E-03	0.43364E-03	0.11507E 03	0.11588E 03
0.28000E 00	0.98957E 02	0.11629E 03	0.71357E-01	0.33464E-04	0.24109E-03	0.43552E-03	0.11506E 03	0.11588E 03
0.28500E 00	0.10072E 03	0.11616E 03	0.67673E-01	0.31735E-04	0.23591E-03	0.43725E-03	0.11505E 03	0.11589E 03
0.29000E 00	0.10249E 03	0.11605E 03	0.64283E-01	0.30148E-04	0.23114E-03	0.43884E-03	0.11505E 03	0.11588E 03
0.29500E 00	0.10426E 03	0.11596E 03	0.61148E-01	0.28676E-04	0.22673E-03	0.44031E-03	0.11504E 03	0.11588E 03
0.30000E 00	0.10603E 03	0.11588E 03	0.58239E-01	0.27313E-04	0.22264E-03	0.44167E-03	0.11504E 03	0.11588E 03
0.30500E 00	0.10779E 03	0.11581E 03	0.55531E-01	0.26043E-04	0.21883E-03	0.44294E-03	0.11504E 03	0.11588E 03
0.31000E 00	0.10956E 03	0.11575E 03	0.53003E-01	0.24858E-04	0.21527E-03	0.44413E-03	0.11503E 03	0.11588E 03
0.31500E 00	0.11133E 03	0.11570E 03	0.50637E-01	0.23748E-04	0.21194E-03	0.44524E-03	0.11503E 03	0.11588E 03
0.32000E 00	0.11309E 03	0.11565E 03	0.48419E-01	0.22708E-04	0.20882E-03	0.44628E-03	0.11503E 03	0.11588E 03
0.32500E 00	0.11486E 03	0.11561E 03	0.46334E-01	0.21730E-04	0.20589E-03	0.44726E-03	0.11503E 03	0.11588E 03
0.33000E 00	0.11663E 03	0.11557E 03	0.44373E-01	0.20810E-04	0.20313E-03	0.44818E-03	0.11503E 03	0.11588E 03
0.33500E 00	0.11839E 03	0.11554E 03	0.42523E-01	0.19943E-04	0.20052E-03	0.44904E-03	0.11502E 03	0.11588E 03
0.34000E 00	0.12016E 03	0.11551E 03	0.40777E-01	0.19124E-04	0.19807E-03	0.44986E-03	0.11502E 03	0.11588E 03
0.34500E 00	0.12193E 03	0.11548E 03	0.39126E-01	0.18349E-04	0.19574E-03	0.45064E-03	0.11502E 03	0.11588E 03
0.35000E 00	0.12370E 03	0.11545E 03	0.37563E-01	0.17616E-04	0.19355E-03	0.45137E-03	0.11502E 03	0.11588E 03
0.35500E 00	0.12546E 03	0.11543E 03	0.36081E-01	0.16922E-04	0.19146E-03	0.45207E-03	0.11502E 03	0.11588E 03
0.36000E 00	0.12723E 03	0.11541E 03	0.34675E-01	0.16262E-04	0.18948E-03	0.45273E-03	0.11502E 03	0.11588E 03
0.36500E 00	0.12900E 03	0.11539E 03	0.33340E-01	0.15635E-04	0.18765E-03	0.45335E-03	0.11502E 03	0.11588E 03
0.37000E 00	0.13076E 03	0.11536E 03	0.32070E-01	0.15045E-04	0.18582E-03	0.45395E-03	0.11502E 03	0.11588E 03
0.37500E 00	0.13253E 03	0.11535E 03	0.30861E-01	0.14474E-04	0.18412E-03	0.45451E-03	0.11502E 03	0.11588E 03
0.38000E 00	0.13430E 03	0.11533E 03	0.29716E-01	0.13934E-04	0.18253E-03	0.45505E-03	0.11501E 03	0.11588E 03
0.38500E 00	0.13607E 03	0.11531E 03	0.28613E-01	0.13419E-04	0.18095E-03	0.45557E-03	0.11501E 03	0.11588E 03
0.39000E 00	0.13783E 03	0.11530E 03	0.27565E-01	0.12928E-04	0.17948E-03	0.45606E-03	0.11501E 03	0.11588E 03
0.39500E 00	0.13960E 03	0.11528E 03	0.26566E-01	0.12455E-04	0.17807E-03	0.45653E-03	0.11501E 03	0.11588E 03
0.40000E 00	0.14137E 03	0.11527E 03	0.25610E-01	0.12011E-04	0.17673E-03	0.45698E-03	0.11501E 03	0.11588E 03
0.40500E 00	0.14313E 03	0.11526E 03	0.24697E-01	0.11583E-04	0.17544E-03	0.45742E-03	0.11501E 03	0.11588E 03
0.41000E 00	0.14490E 03	0.11525E 03	0.23823E-01	0.11173E-04	0.17421E-03	0.45781E-03	0.11501E 03	0.11588E 03
0.41500E 00	0.14667E 03	0.11524E 03	0.22987E-01	0.10781E-04	0.17304E-03	0.45821E-03	0.11501E 03	0.11588E 03
0.42000E 00	0.14844E 03	0.11523E 03	0.22186E-01	0.10485E-04	0.17191E-03	0.45858E-03	0.11501E 03	0.11588E 03
0.42500E 00	0.15020E 03	0.11522E 03	0.21418E-01	0.10345E-04	0.17083E-03	0.45894E-03	0.11501E 03	0.11588E 03
0.43000E 00	0.15197E 03	0.11521E 03	0.20682E-01	0.96995E-05	0.16979E-03	0.45929E-03	0.11501E 03	0.11589E 03
0.43500E 00	0.15374E 03	0.11520E 03	0.19975E-01	0.93682E-05	0.16880E-03	0.45962E-03	0.11501E 03	0.11588E 03
0.44000E 00	0.15550E 03	0.10351E 03	0.19295E-01	0.90594E-05	0.16785E-03	0.45994E-03	0.46654E 01	0.88588E 00

APPENDIX G

Reaction Kinetics

A series of batch reactor runs[1,2] was made to obtain kinetic data on the synthesis of TVOPA and A-3. For both reactions the data were successfully correlated on the assumption of a seco .d order reaction mechanism. The Arrhenius plots based upon this correlation are shown in Fig. 8.

[1]Rohm & Haas Company, Quarterly Progress Report on Chemical and Propellant Processing, No. P-64-3, February 15 1965.

[2]Ibid, No. P-64-17, August 15, 1964.

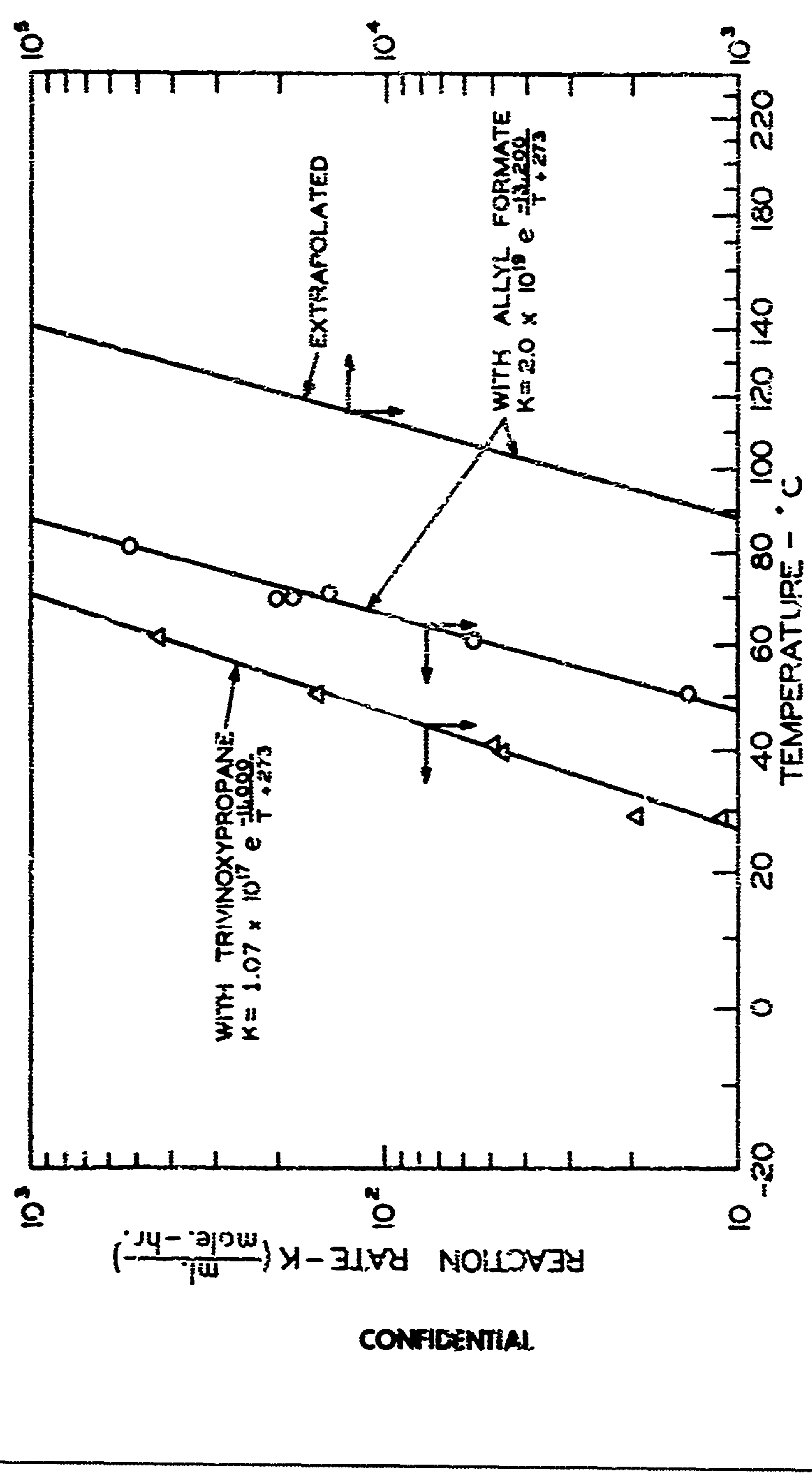

FIG. 8 ARRHENIUS PLOT FOR A-3 AND TVOPA LIQUID PHASE REACTION

APPENDIX H

N_2F_4 Solubility

A series of N_2F_4 solubility determinations was made by the Physical Chemistry Group, and the results are shown in Table V. The solubility of N_2F_4 in Freon TF and mixed solvent at temperatures from 40-100°C and a total pressure of 300 psia is shown in Fig. 9. Minimum reactor pressure was selected from these values to avoid partial gassing in the first stage of the reactor. For example, the minimum pressure for A-3 synthesis was 415 psia for the 0.204 grams N_2F_4/cc solvent input since the N_2F_4 solubility in mixed solvent was found to be 0.213 at 100°C.

Table V

N_2F_4 Solubility in Various Solvents

Solvent	Temp. °C	Pressure (psi abs.)	Solubility gm N_2F_4/cc solvent
Freon TF	40	50	.036
	40	100	.139
	40	150	.200
	40	200	.377
	40	300	.869
	60	50	.005
	60	100	.073
	60	200	.213
	60	300	.463
	80	300	.215
$ChCl_3$	40	300	.274
	60	300	.162
	80	300	.102
Freon TF:$CHCl_3$, 4:1 by vol.	40	300	.724
	60	300	.361
	80	300	.241
	100	300	.112
	100	300	.104
	100	415	.213
Freon TF:CH_2Cl_2, 3:1 by vol.	40	50	.035
	40	50	.023
	40	100	.092
	40	150	.183
	40	200	.271
1,2-dichloroethane	40	300	.052
	40	300	.045
1,1,2-trichloroethane	40	300	.032
	40	300	.041
H_2O	30	150	.002

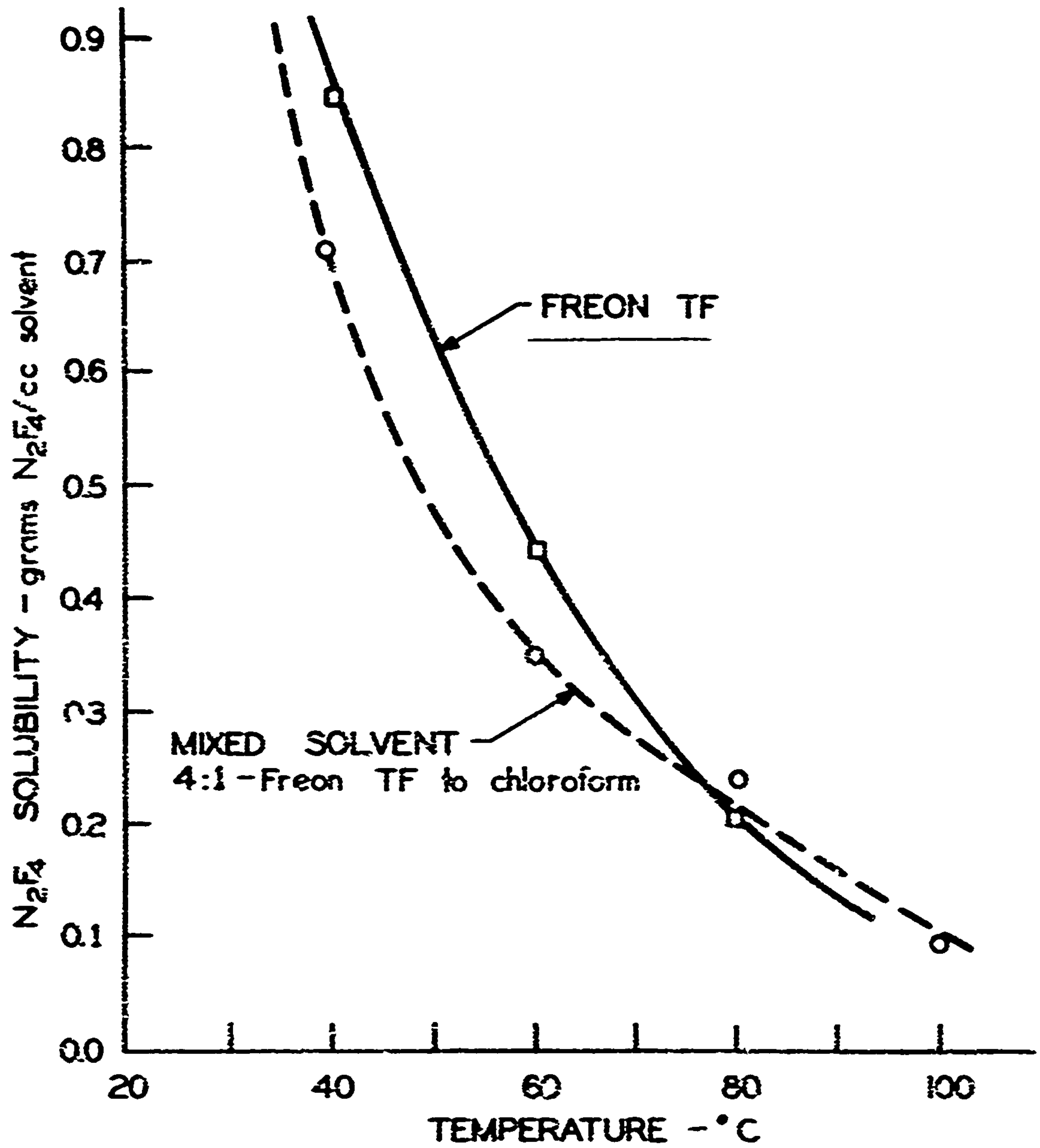

FIG. 9 N_2F_4 SOLUBILITY IN FREON TF AND MIXED SOLVENT VERSUS TEMPERATURE AT 300 PSIA TOTAL PRESSURE

APPENDIX I

Corrosion Studies

A single corrosion experiment with > 97% N_2F_4 showed corrosion rates of about 10^{-4} inches per year with Hastelloy C, type 440 stainless steel, and nickel, and about 10^{-5} inches per year with type 316 stainless steel. Exposure was to N_2F_4 free of HF under the test conditions shown in Table VI. The results, summarized in Table VII, showed that all of the materials tested were acceptable for construction and the type 316 stainless steel could be used for precision fitted parts.

The test coupons were about 3/4 x 3/8 x 1/16 inches and were suspended by Teflon string in a 30 ml test cell located downstream of the compressor second stage discharge. About 10% of the N_2F_4 exposure was at > 300 psig and the remainder in the range of 0-30 psig. Exposure was not continuous because equipment changes required periodic flushing with nitrogen and air for personnel entry into the reactor bay.

Table VI

Corrosion Test Conditions

Test	
Exposure, hours	
30 psig N_2F_4	1169
300-500 psig N_2F_4	133
Temperature, °C	35-42
Analysis (Average), %	
N_2F_4	> 97%
NO	< 3%
HF	≈ 0%

Table VII

Summary of Corrosion Tests on N_2F_4

Sample	Corrosion Rate, inches/yr.
Hastelloy C	1.3×10^{-4}
440 Stainless Steel	1.8×10^{-4}
316 Stainless Steel	1.4×10^{-5}
Nickel	2.6×10^{-4}

The coupons were prepared by successive washing with water, acetone, and methylene chloride. Two weighings were made following exposure. The first was made after the coupons were washed by the above procedure, and the second followed a Bon Ami scouring to remove surface films. No additional weight loss was observed after scouring. Estimated error of the corrosion rate was ±50%, based upon the accuracy of the balance used to determine the weight loss (excepting 316 stainless steel which was ±100%).

APPENDIX J

Safety

N_2F_4 Cylinder Decomposition

About 4 pounds of N_2F_4 (in a single cylinder) was lost because of partial decomposition upon opening of the main cylinder valve. About 13% of the N_2F_4 decomposed to NF_3 and N_2 by the overall reaction:

$$3\ N_2F_4 \longrightarrow 4\ NF_3 + N_2;$$

$$\Delta H_R = -38.85\ \frac{\text{kcal}}{\text{mol } N_2F_4}$$

Following a routine procedure, the main cylinder valve was manually "cracked" to bleed the N_2F_4 into the manifold. The pressure momentarily leveled off at 130 psig and then started rising to 150 psig. Immediately afterwards the operator noticed that the top of the cylinder was "uncomfortably" hot to the touch (ca. 130°F). The incident was particularly disconcerting since the valve had already been opened and closed once to obtain a mass spectral sample.

Previous studies[1] of explosive N_2F_4 reactions indicated a maximum pressure increase of about 14 times the initial pressure (using exploding wire or No. 6 detonators for initiation). These studies were the basis of the 130 psig limit on a standard nitrogen cylinder fitted with an oxygen main valve. Although in this incident the protection offered by the cylinder was adequate, an additional safety factor was later incorporated into the N_2F_4 handling procedure by providing for remote opening and closing of the main cylinder valve.

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[1]Rohm & Haas Company, Quarterly Progress Report on Interior Ballistics, P-60-13, pp. 1-7, January 19, 1961.

A possible cause of the incident was the initiation of the N_2F_4 by air. Since this incident two cylinders from the same shipment (out of six received) have leaked N_2F_4 during the opening procedure because the stem packing was inadequate. These are the first cylinders with which this difficulty was observed; however, leaks of this kind are not easy to detect because there are valve positions in which sealing does occur. Past experience suggested that, once initiated, the reaction could propagate back through the leak. Leakage is a problem only during opening or closing using the standard practice of tightening the valve in the full open position, because there is a superior second seal independent of the stem seal. For this reason personnel exposure to full N_2F_4 cylinders was permitted when the valve was fully opened or closed.

Explosions in Reactor

Six explosions occurred during operation of the liquid phase flow reactor. Four occurred without warning in the mixing tee (where the N_2F_4 was added to the olefin solution), and two occurred during attempts to eliminate reactor plugs. There was no evidence of propagation through the condensed liquid lines; however, in two instances there was propagation through the 1/8" I. D. N_2F_4 feed tube. Equipment damage was minor, being limited to the mixing tee, a valve, or the tubular reactor coils. Down time for repairs was usually two to three days.

The four explosions in the mixing tee were similar. In each instance no difficulties had been encountered, and all measurements suggested the reactor was operating normally when the explosion occurred. In the first two explosions there was propagation back to the N_2F_4 feed valve. Following the first two incidents, the N_2F_4 feed tube was inserted into the cooled section to insure absorption where the 0.18" I. D. tube was totally surrounded by the 0°C brine bath. This modification limited damage to the mixing tee in the two subsequent incidents.

Apparently the explosions were not related to N_2F_4 purity, which varied from 97 to 99.5%. A probable cause was initiation by a small amount of air inadvertently introduced with the solvent-olefin feed. Observations confirmed that the air purge technique did not eliminate air in the 30 ml section between the glass wool filter and the suction side of the liquid pump, and as passage through the filter became difficult the pump started taking a little air with each stroke.

The two other explosions were related to reactor plugging which forced premature shut down of the plant. Both occurred during attempts to remove the solid plug so that the N_2F_4 could be cleaned out to allow personnel entry into the reactor bay. The explosions were assumed to be caused by locally excessive N_2F_4 concentrations reacting with either the solids or olefin.